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ROYALTY EVALUATION PROCEDURE

OF THE

PROTOTYPE OIL SHALE LEASES

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ROYALTY EVALUATION PROCEDURE

OF THE

PROTOTYPE OIL SHALE LEASES

OIL SHALE OFFICE
CENTRAL

United States Department of the Interior

Geological Survey, Conservation Division

Area Oil Shale Supervisor's Office

May 1980

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U. S. Geological Survey
Conservation Division
Area Oil Shale Supervisor's Office
131 N. 6th, Suite 300
Grand Junction, Colorado 81501

ABSTRACT

The method of computing the royalty for the prototype oil shale lease tracts is dependent on whether the oil shale is processed by an in situ method or whether the oil shale is mined and then retorted above ground.

If the oil shale is mined and processed or sold, the basic royalty rate is equal to twelve cents a ton for an oil content of thirty gallons per ton. Royalty is adjusted by the oil content and ratio of the combined average value per barrel of all crude oil and crude shale oil produced in the states of Colorado, Utah, and Wyoming for the preceeding year and base year. The base price is the average crude oil price of the three state area in 1974 when the leases were signed.

If the oil shale is processed by in situ methods, the basic royalty rate is equal to twelve cents per equivalent ton. Equivalent tons are based on the total gross heat of combustion in BTU's of all oil and gas products at the wellhead or shaft openings. The royalty is only adjusted by the variance of crude oil prices, but not shale oil grade because the equivalent tons are calculated on a shale oil content of thirty gallons per ton.

The lease requires an additional royalty for all minerals other than oil shale contained in oil shale produced from the leased deposit. This royalty is to be computed on a percentage of the gross value of the other minerals at the point of shipment to market.

To expedite the development of the lease tracts, there is a minimum royalty required of the lessees. This royalty can be offset with expenditures which are directly attributable to operations for the development of the lease deposits through the tenth lease year.

INTRODUCTION

Of all the hydrocarbon resources in the world, the most abundant single resource in one area is the oil shale deposit contained in the Green River Formation in the three-state area of Colorado, Utah, and Wyoming. It is estimated to contain more than 2.4 trillion barrels of oil equivalent of which 1.8 trillion barrels are classed as identified resources.[1/] When the organic matter (called kerogen) in oil shale is heated to 800 to 900° F, the kerogen will decompose into shale oil, carbonaceous residue, and gas.

In 1974, the U. S. Department of Interior leased four 5,000-acre tracts for commercial oil shale development under the Prototype Oil Shale Program. The program was designed to provide a new energy source, to protect the environment of the prototype areas, to permit a fair return to all, and to develop expertise in oil shale management and technology.

Federal oil shale lease tracts C-a (Rio Blanco Oil Shale Company) and C-b (Cathedral Bluffs Shale Oil Company) are in the Piceance Basin of northwestern Colorado; tracts U-a and U-b (White River Shale Project) are in the adjoining Uinta Basin of eastern Utah (Fig. 1). Present plans call for development of the Colorado tract C-b by the modified in situ retorting processes, Colorado tract C-a by combined modified in situ and aboveground

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1/ United States Mineral Resources, 1973, Geological Survey Professional Paper 820, p. 500.

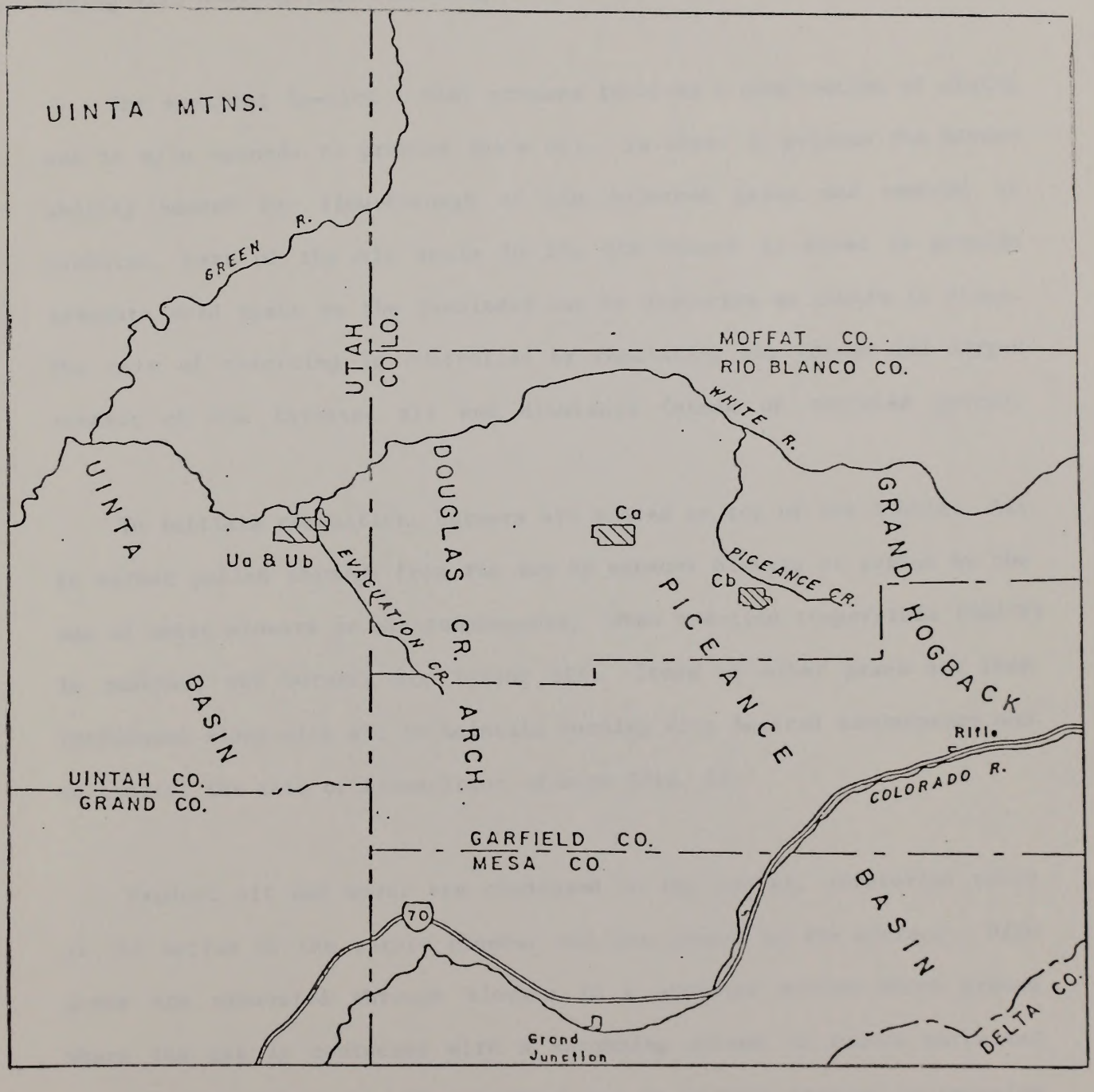


Figure 1.--Location of prototype oil-shale lease tracts C-a, C-b, U-a and U-b.

retorting, and for development of the two Utah tracts by room-and-pillar mining with above-ground retorting.

The modified in-situ (MIS) process involves a combination of mining and in situ methods to produce shale oil. In order to produce the permeability needed for flow-through of the injected gases and removal of products, part of the oil shale in the MIS retort is mined to provide adequate void space so the remainder can be converted to rubble in place. The rate of retorting is controlled by regulating the volume and oxygen content of the injected air and dilutants (steam or recycled gases).

To initiate combustion, burners are placed on top of the rubble. Air is either pulled through from the top by exhaust blowers or pushed by the use of inlet blowers or air compressors. When reaction temperature (900°F) is reached, the burners are turned off. Steam or other gases are then introduced along with air to maintain burning at a desired temperature and to control the rate of flame-front advance (Fig. 2).

Product oil and water are condensed on the cooler, unretorted shale at the bottom of the retort chamber and are pumped to the surface. Off-gases are exhausted through blowers to a scrubber system above ground where the gas is contacted with a scrubbing stream to remove entrained dust and oil particles. The scrubbed gas is further treated by removing the oil and water by compression and by reduction of the sulfur compounds. Purified gas is then used for steam production or possibly gas turbine-powered electric generators.

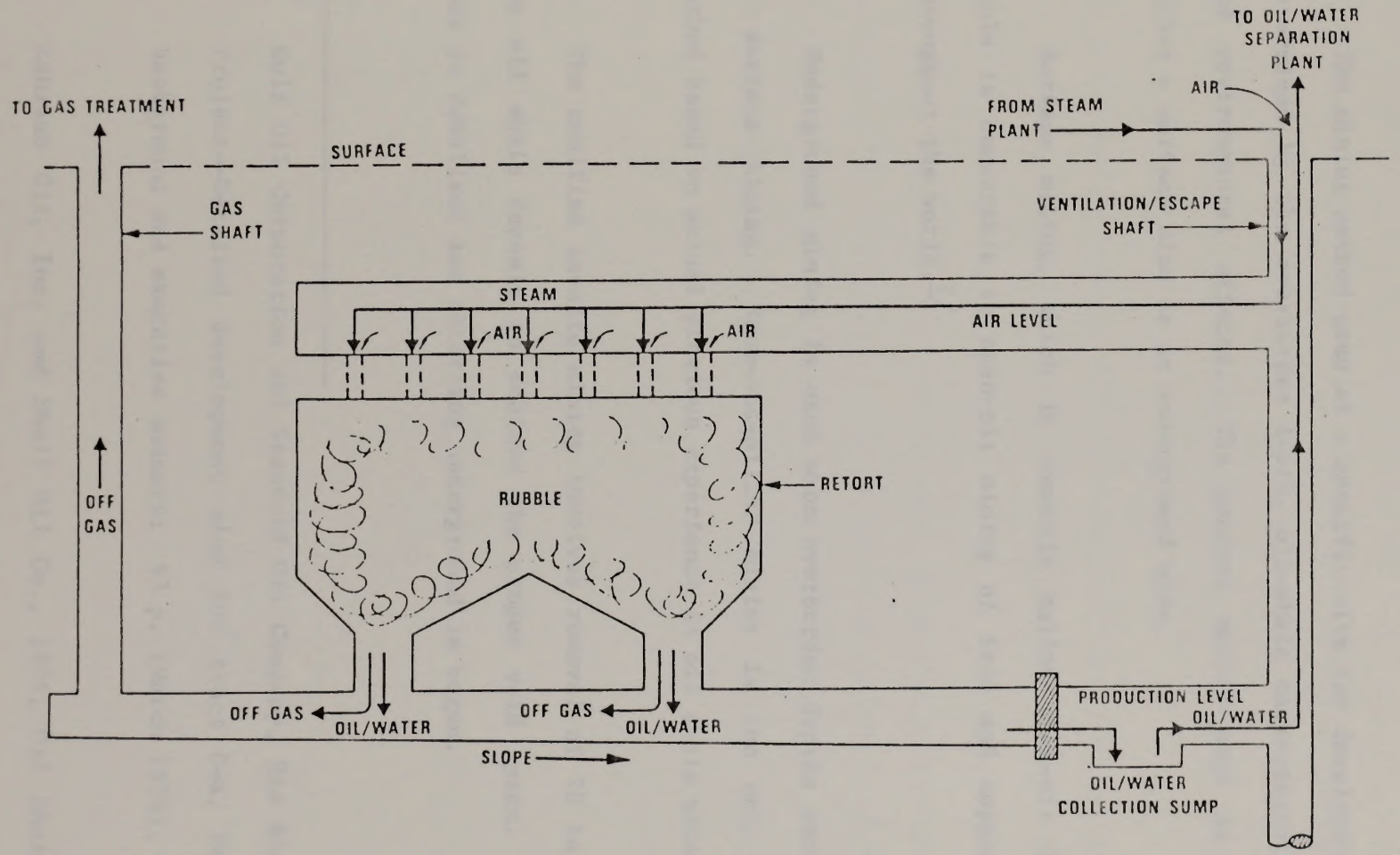
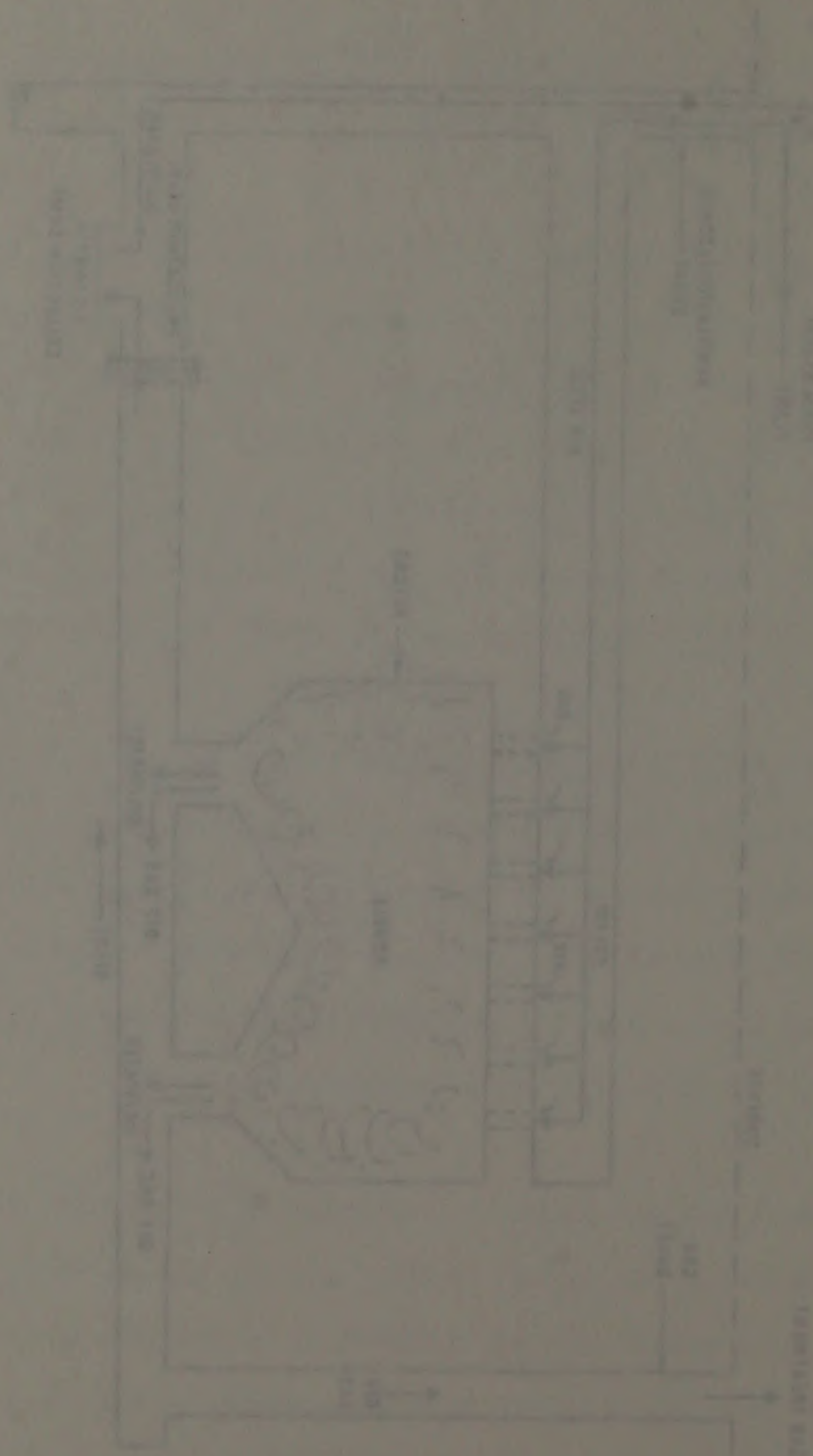


Figure 2.--Schematic diagram of a modified in-situ retort and related air and production mine levels (Ashland Colorado, Inc., and Occidental Oil Shale, Inc., 1977).



The mining method used at a specific site for developing oil shale is determined by the overburden depth, oil-shale characteristics, economics and environmental effects. The general method used is classified as either a surface mine or an underground mine.

Surface mining, which is commonly called open-pit mining, of oil shale is comparable to open-pit mining of iron and copper as practiced throughout the world.[2/]

Underground mining is used when overburden depths exceed the limits of surface mining. Room-and-pillar mining is the only proven mining method based on actual previous experience in oil shale mines.[3/]

The modified in-situ mining involves removal of 20 to 40 percent of the oil shale deposit to achieve the proper void space. The remaining rock is rubblized and retorting underground is begun.

2/ Gulf Oil Corporation and Standard Oil Company, Rio Blanco Oil Shale Project--Detailed development plan for tract C-a, Vol. 1, Project background and executive summary: 83 p. (March 1976).

3/ Ashland Oil, Inc. and Shell Oil Co., 1976, Oil Shale Tract C-b - Detailed development plan and related materials: 2v. (Chapters in each volume separately paginated.) (Feb. 1976)

There are basically two types of above ground retorts:

(1) a direct-heated retort where air is injected into a moving bed of crushed shale to support combustion and supply process heat, and

(2) an indirect-heated retort which gets heat from an external source of hot gases or hot solids.

Computation of the royalty that is to be collected from resource recovery of the prototype oil shale leases is dependent on whether the oil shale is processed by an in-situ method or whether oil shale is mined and then retorted above ground.

PURPOSE AND OBJECTIVES

The purpose and objectives of this paper are to provide guidelines and procedures for submittal, evaluation and approval of royalty due the Geological Survey of the U. S. Department of the Interior. The lessee must determine the royalty and pay the amount due on a monthly basis. Verification of the data will be done by periodic audits, inspections, and operational data calculations as per program goals and lease[4/] terms.

Figure 3 depicts a simplified flow of how the royalty will be determined for the oil shale tracts. See the lease requirements section for more detail.

4/ U. S. Bureau of Land Management, 1973. Modification of an oil shale withdrawal in Colorado, Utah, Wyoming. Federal Register 38:230, pp. 33186-33199 (November 30, 1973).

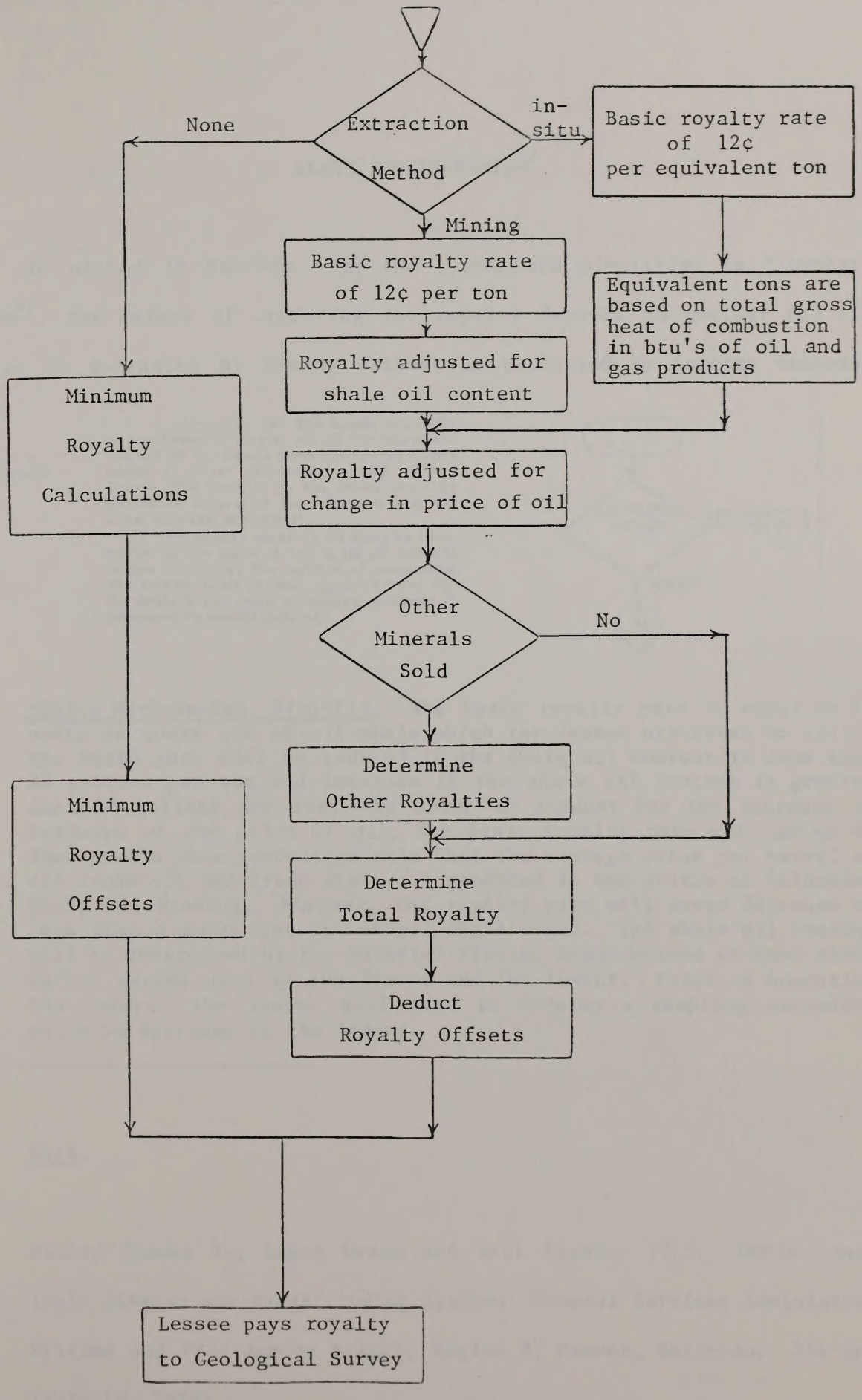
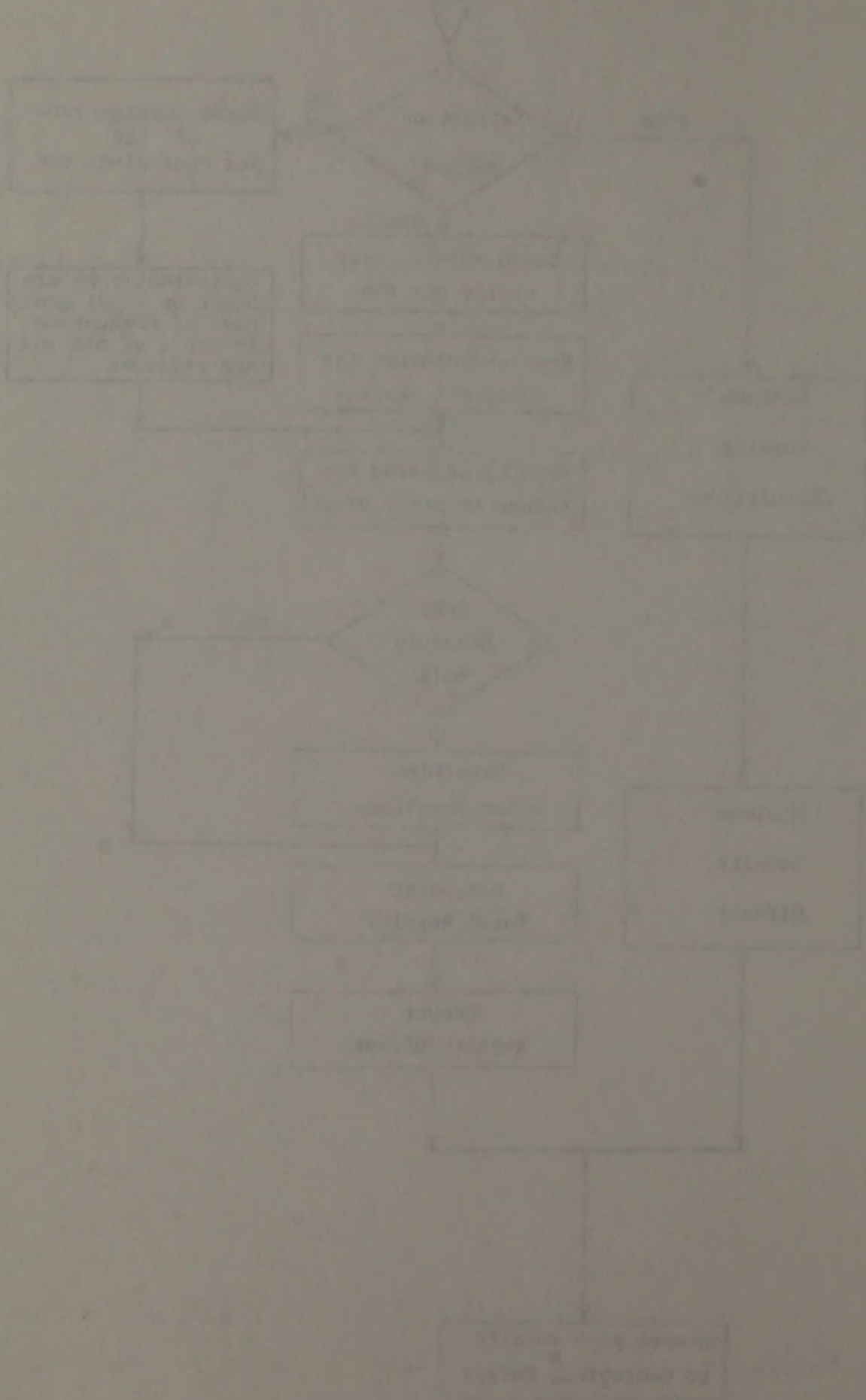

Extraction Method
None
in-situ
Mining
Basic royalty rate of 12¢ per equivalent ton
Basic royalty rate of 12¢ per ton
Equivalent tons are based on total gross heat of combustion in btu's of oil and gas products
Royalty adjusted for shale oil content
Minimum Royalty Calculations
Royalty adjusted for change in price of oil
Other Minerals Sold
No
Determine Other Royalties
Minimum Royalty Offsets
Determine Total Royalty
Deduct Royalty Offsets
Lessee pays royalty to Geological Survey

Figure 3. -- Simplified diagram of royalty determinations.



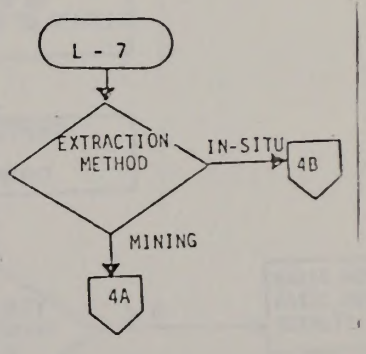
LEASE REQUIREMENTS[5/]

As stated in Section 7 of the Lease, and simplified in flowchart form[6/], the method of computing the royalty depends on whether the oil shale is extracted by mining methods or processed by in-situ methods.

Sec. 7.

Royalties. (a) The Lessee shall pay to the Lessor a royalty on all Oil Shale extracted by the Lessee from the Leased Lands which is either processed or sold by the Lessee. The royalty on Oil Shale shall be computed separately for shale oil and for other minerals as follows:

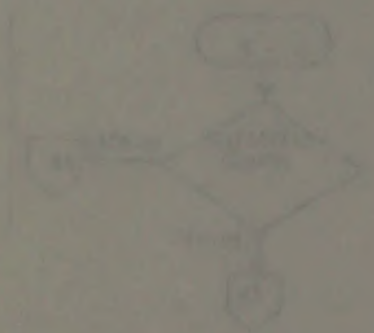
(1) The royalty on shale oil shall be computed on the basis of the shale oil content of the Oil Shale; the method of computing the royalty shall depend upon whether the Oil Shale is extracted by mining methods or processed by *in situ* methods.



Mining Methods-Sec. 7(a)(1)i. The basic royalty rate is equal to 12 cents on every ton of oil shale which the lessee processes or sells. The basic rate will be reduced if the shale oil content is less than 30 gallons per ton and increase if the shale oil content is greater than 30 gallons per ton. In order to account for the increase or decrease of the price of oil, the basic royalty rate will go up or down at the same percentage rate that the average value per barrel of all crude oil and crude shale oil produced in the states of Colorado, Utah, and Wyoming. However, the royalty rate will never decrease to less than 4 cents per ton of oil shale mined. The shale oil content will be determined by the Modified Fischer Assay Method or some other method agreed upon by the lessee and the lessor. Prior to operating the retort, the lessee will have to develop a sampling procedure which is approved by the lessor.

5/ Ibid.

6/ Blair, Thomas J., Laura Grace and Earl Elmore, 1975. OSMIS lease logic diagram and manual coding system. General Services Administration, Systems and Programming Branch, Region 8, Denver, Colorado. 254 pp. (July 15, 1975)



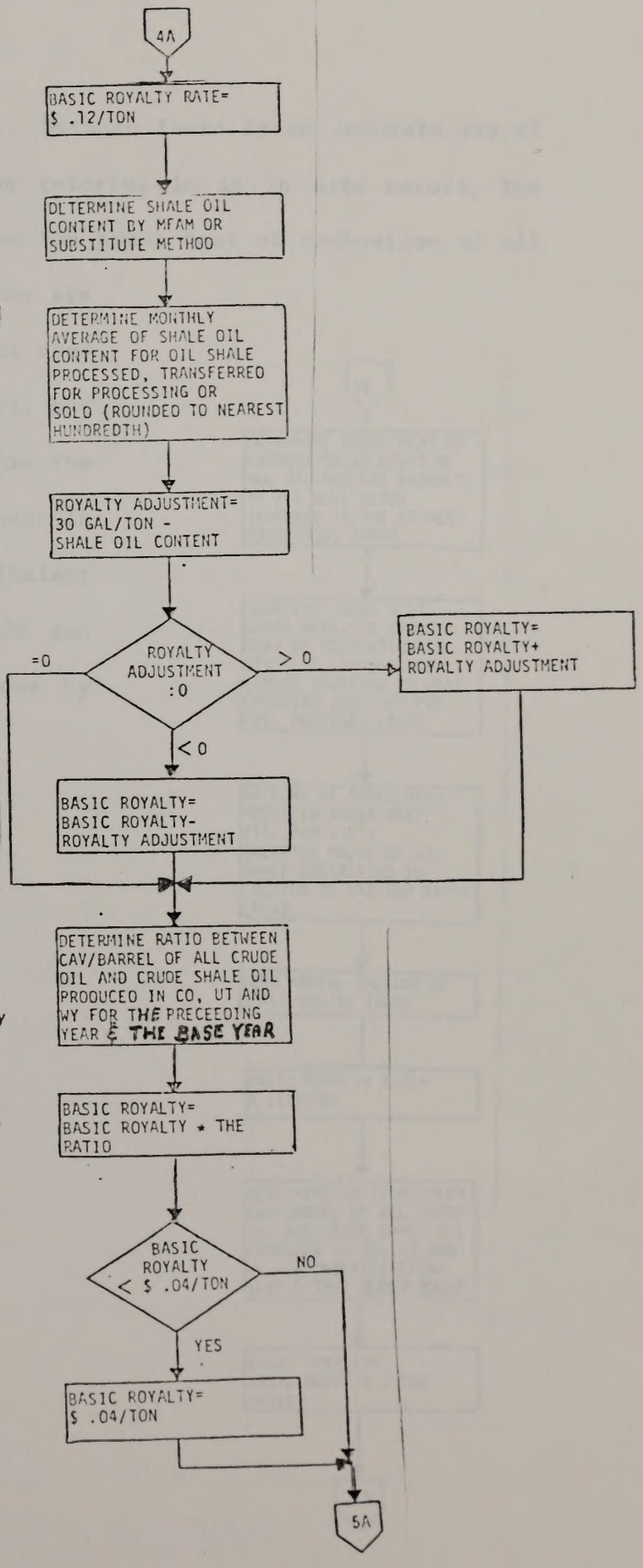
Sec. 7(a)(1)(i)

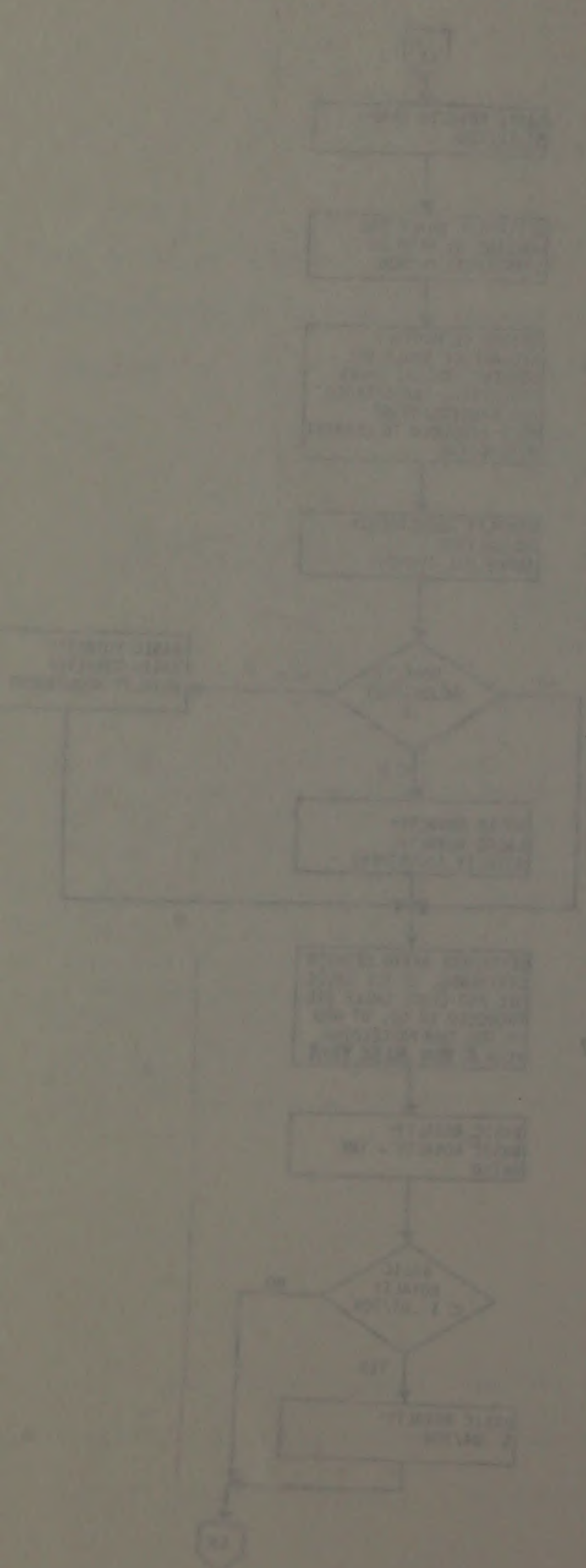
If the Oil Shale is extracted by mining methods, the Lessee shall pay the Lessor a basic royalty rate of 12 cents on every Ton of Oil Shale which the Lessee either processes under this Lease either on or off the Leased Lands or sells prior to processing. This basic royalty rate shall be subject to the following adjustments:

(A) If the shale oil content of the Oil Shale mined is less than 30 gallons per Ton, the basic royalty rate per Ton of Oil Shale shall be reduced by one cent for each gallon or fraction thereof that the shale oil content is less than 30 gallons per Ton, but in no event shall the royalty rate be less than four cents per Ton. If the shale oil content of the Oil Shale mined is more than 30 gallons per Ton, the basic royalty rate per Ton shall be increased by one cent for each gallon or fraction thereof that the shale oil content is more than 30 gallons per Ton.

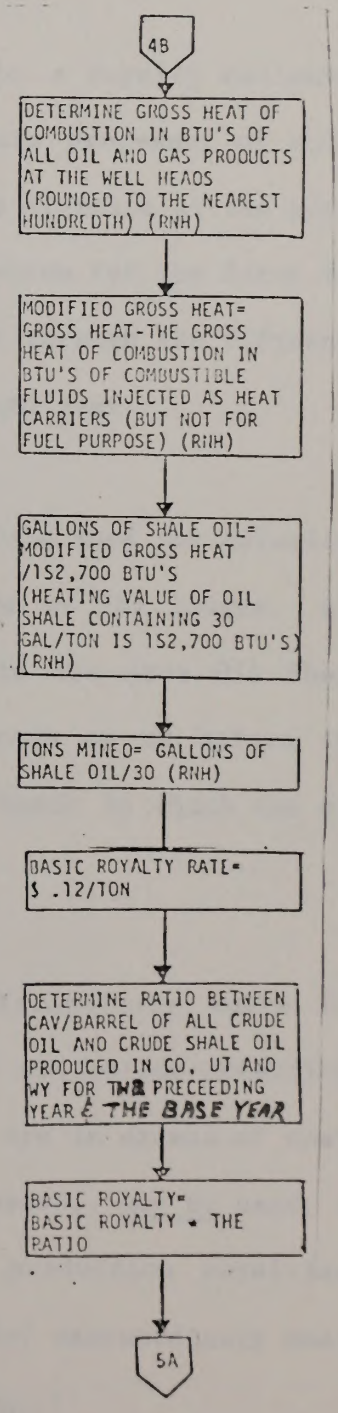
(B) For the calendar year in which the Effective Date occurs and for each calendar year thereafter, the Secretary shall determine the combined average value per barrel of all crude oil and crude shale oil produced in the States of Colorado, Utah, and Wyoming. The basic royalty rate applicable to the second and each succeeding Lease Year shall be adjusted by an increase or decrease of the same percentage as the percentage of increase or decrease in the combined average value for the calendar year during which that Lease Year begins as compared with the combined average value for the calendar year during which the previous Lease Year began. However, in no event shall the basic royalty rate for shale oil be decreased to less than 4 cents on every Ton of Oil Shale mined under the lease.

(C) The shale oil content of the Oil Shale shall be determined either by the Modified Fischer Assay method or by such other method as the Lessor and the Lessee adopt, and the royalty shall be based on the monthly average of shale oil content of all Oil Shale processed under this lease or transferred from the Leased Lands for processing or sale ~~or~~ by the Lessee. Computations of quantities, assays and royalties shall be rounded to the nearest hundredth, or within the limits of the standard deviation for commercial testing equipment as approved by the Mining Supervisor.


4A
BASIC ROYALTY RATE= $ .12/TON
DETERMINE SHALE OIL CONTENT BY MFAM OR SUBSTITUTE METHOD
DETERMINE MONTHLY AVERAGE OF SHALE OIL CONTENT FOR OIL SHALE PROCESSED, TRANSFERRED FOR PROCESSING OR SOLD (ROUNDED TO NEAREST HUNDREDTH)
ROYALTY ADJUSTMENT= 30 GAL/TON - SHALE OIL CONTENT
ROYALTY ADJUSTMENT : 0
=0
> 0
< 0
BASIC ROYALTY= BASIC ROYALTY+ ROYALTY ADJUSTMENT
BASIC ROYALTY= BASIC ROYALTY- ROYALTY ADJUSTMENT
DETERMINE RATIO BETWEEN CAV/BARREL OF ALL CRUDE OIL AND CRUDE SHALE OIL PRODUCED IN CO, UT AND WY FOR THE PRECEEDING YEAR & THE BASE YEAR
BASIC ROYALTY= BASIC ROYALTY * THE RATIO
BASIC ROYALTY < $ .04/TON
NO
YES
BASIC ROYALTY= $ .04/TON
5A



In Situ Methods-Sec. 7(a)(1)ii. Because there is no accurate way of determining the amount of tons retorted in an in situ retort, the royalty will be determined from the gross heat of combustion of all oil and gas products before they are treated or refined. Any product used as a heat carrier to the retort, but not fuel, may be deducted from the total gross heat. The gross heat in BTU's may be changed to equivalent gallons by dividing by 152,700 and then changed to equivalent tons by dividing by 30.


4B
DETERMINE GROSS HEAT OF COMBUSTION IN BTU'S OF ALL OIL AND GAS PRODUCTS AT THE WELL HEADS (ROUNDED TO THE NEAREST HUNDREDTH) (RNH)
MODIFIED GROSS HEAT= GROSS HEAT-THE GROSS HEAT OF COMBUSTION IN BTU'S OF COMBUSTIBLE FLUIDS INJECTED AS HEAT CARRIERS (BUT NOT FOR FUEL PURPOSE) (RNH)
GALLONS OF SHALE OIL= MODIFIED GROSS HEAT /152,700 BTU'S (HEATING VALUE OF OIL SHALE CONTAINING 30 GAL/TON IS 152,700 BTU'S) (RNH)
TONS MINED= GALLONS OF SHALE OIL/30 (RNH)
BASIC ROYALTY RATE= $ .12/TON
DETERMINE RATIO BETWEEN CAV/BARREL OF ALL CRUDE OIL AND CRUDE SHALE OIL PRODUCED IN CO, UT AND WY FOR THE PRECEEDING YEAR & THE BASE YEAR
BASIC ROYALTY= BASIC ROYALTY • THE RATIO
5A

Sec. 7(a)(1)(ii)

(A) If the Oil Shale is processed by *in situ* methods, royalty shall be paid at a basic royalty rate of 12 cents per Ton. The number of Tons processed shall, for purposes of computing royalty, be determined by: (I) establishing through calorimetric tests designated by the American Society for Testing and Materials as "Standard" or "Tentative," the total gross heat of combustion in BTUs of all oil and gas products at the well head, adjusted downward by the total gross heat of combustion in BTUs of combustible fluids (gases or liquids) injected as heat carriers, but not for fuel purposes, into the formation being processed; (II) dividing the adjusted total gross heat of combustion in BTUs by 152,700 BTUs (shale oil and gas recovered by Modified Fischer Assay of Oil Shales, containing approximately 30 gallons of shale oil per Ton, has a heating value of 152,700 BTUs per gallon of shale oil and associated gas), to arrive at the equivalent number of gallons of shale oil produced; and (III) dividing the equivalent number of gallons of shale oil produced by 30, to arrive at the number of Tons of Oil Shale processed by *in situ* methods.

(B) The basic royalty rate applicable to shale oil from Oil Shale process by *in situ* methods shall be adjusted in the same manner as that provided in paragraph (a)(1)(i)(B) of this section for the adjustment of the basic royalty rate applicable to shall oil processed from Oil Shale extracted by mining methods.

(C) Computations of quantities, assays and royalties relating to tonnage of Oil Shale shall be determined by the same standards as used under Section 7 (a)(1)(i)(C).

The basic royalty rate for in situ methods is 12 cents per equivalent ton retorted. The royalty rate is then adjusted for oil price changes by multiplying by the index factor ratio as explained in the mining method.

Mineral Royalties-Sec. 7(a)(2). There shall be a royalty collected on all minerals other than shale oil which are processed or sold. The royalty shall be based on the value of the minerals at the point of shipment to the market. The rate is 3 percentum for the first ten lease years, 4 percentum for the eleventh year through the fifteenth year and 5 percentum beginning with the sixteenth year.

Data Collection and Payments-Sec. 7(b) 7(c). Data used for calculating royalty will be placed in books and preserved by the lessee. All such data and books will be made available to the Area Oil Shale Supervisor. Payments for royalties will be made on or before the last day of the month following the calendar month in which the oil shale is processed or sold.

Extraordinary Cost Offsets-Sec. 7(d). Any extraordinary costs for compliance with requirements for environmental protection prescribed in approved Detailed Development Plans, which are in excess of costs contemplated by the parties at the time of approval, may be used, at the discretion of the Secretary, to offset production royalties. (See Lease environmental stipulation 11(L)(3) for extraordinary costs related to development of revegetation technology.)

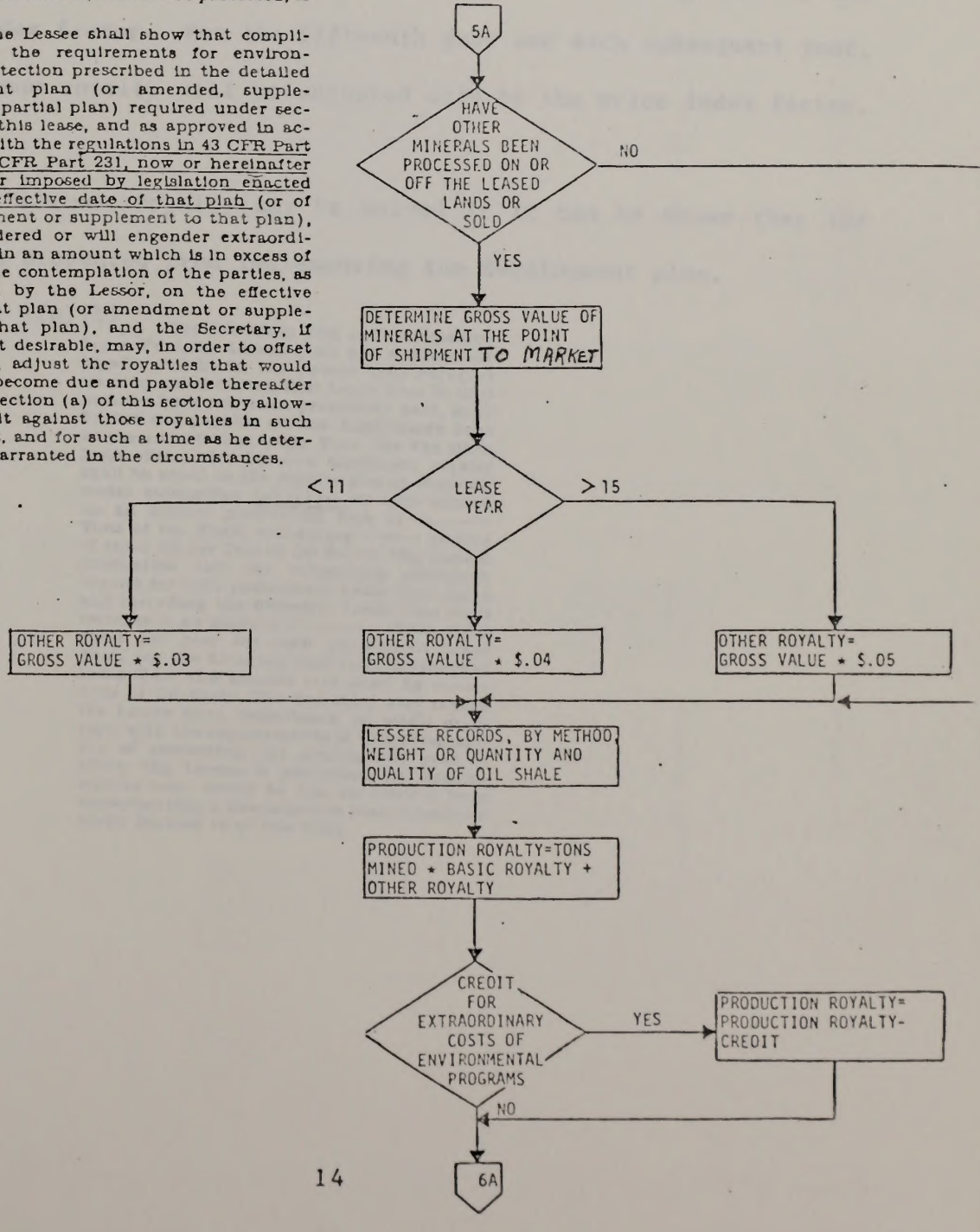
Sec. 7(a)(2).

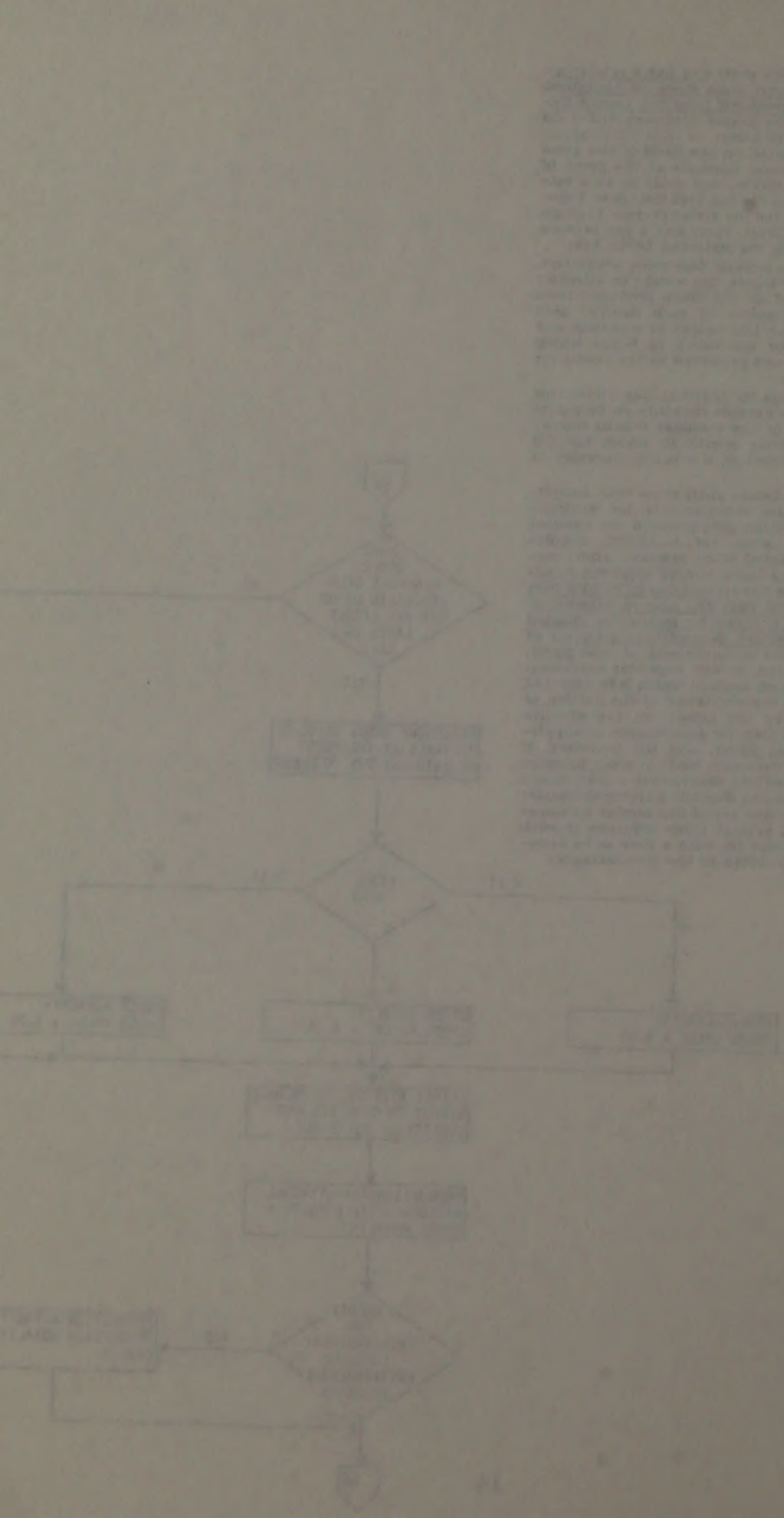
The Lessee shall also pay a royalty on all minerals other than shale oil contained in Oil Shale produced from the Leased Deposits which the Lessee processes, either on or off the Leased Lands, or sells. This royalty shall be computed on the basis of the gross value of the other minerals at the point of shipment to market, and shall be at a rate of 3 per centum for the first ten Lease Years, 4 per centum for the eleventh year through the fifteenth Lease Year, and 5 per centum beginning with the sixteenth Lease Year.

(b) The Lessee shall determine accurately, on the Leased Lands, the weight or quantity and quality of all Oil Shale produced from the Leased Deposits by each method used and shall enter the weight or quantity and quality thereof accurately in books which shall be kept and preserved by the Lessee for such purposes.

(c) Payments for royalties due under this lease shall be payable monthly on or before the last day of the calendar month following the calendar month in which the Oil Shale is processed or, if it is not processed, is sold.

(d) If the Lessee shall show that compliance with the requirements for environmental protection prescribed in the detailed development plan (or amended, supplemental, or partial plan) required under section 10 of this lease, and as approved in accordance with the regulations in 43 CFR Part 23 and 30 CFR Part 231, now or hereinafter in force, or imposed by legislation enacted after the effective date of that plan (or of an amendment or supplement to that plan), has engendered or will engender extraordinary costs in an amount which is in excess of those in the contemplation of the parties, as determined by the Lessor, on the effective date of that plan (or amendment or supplement to that plan), and the Secretary, if he deems it desirable, may, in order to offset such costs, adjust the royalties that would otherwise become due and payable thereafter under subsection (a) of this section by allowing a credit against those royalties in such an amount, and for such a time as he determines is warranted in the circumstances.

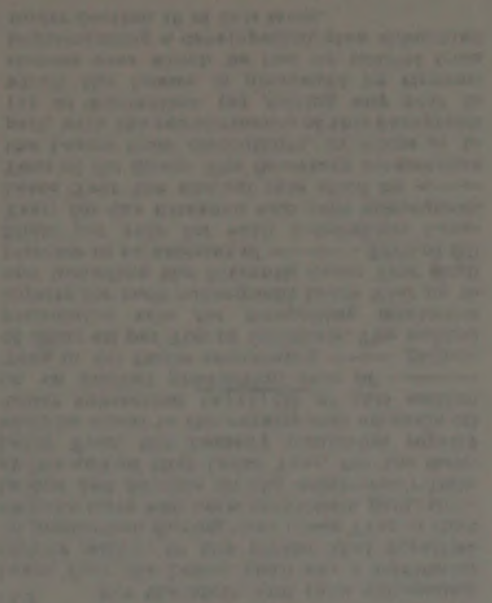

5A
HAVE OTHER MINERALS BEEN PROCESSED ON OR OFF THE LEASED LANDS OR SOLD
NO
YES
DETERMINE GROSS VALUE OF MINERALS AT THE POINT OF SHIPMENT TO MARKET
LEASE YEAR
<11
>15
OTHER ROYALTY= GROSS VALUE * $.03
OTHER ROYALTY= GROSS VALUE * $.04
OTHER ROYALTY= GROSS VALUE * $.05
LESSEE RECORDS, BY METHOD, WEIGHT OR QUANTITY AND QUALITY OF OIL SHALE
PRODUCTION ROYALTY=TONS MINED * BASIC ROYALTY + OTHER ROYALTY
CREDIT FOR EXTRAORDINARY COSTS OF ENVIRONMENTAL PROGRAMS
YES
PRODUCTION ROYALTY= PRODUCTION ROYALTY- CREDIT
NO
6A

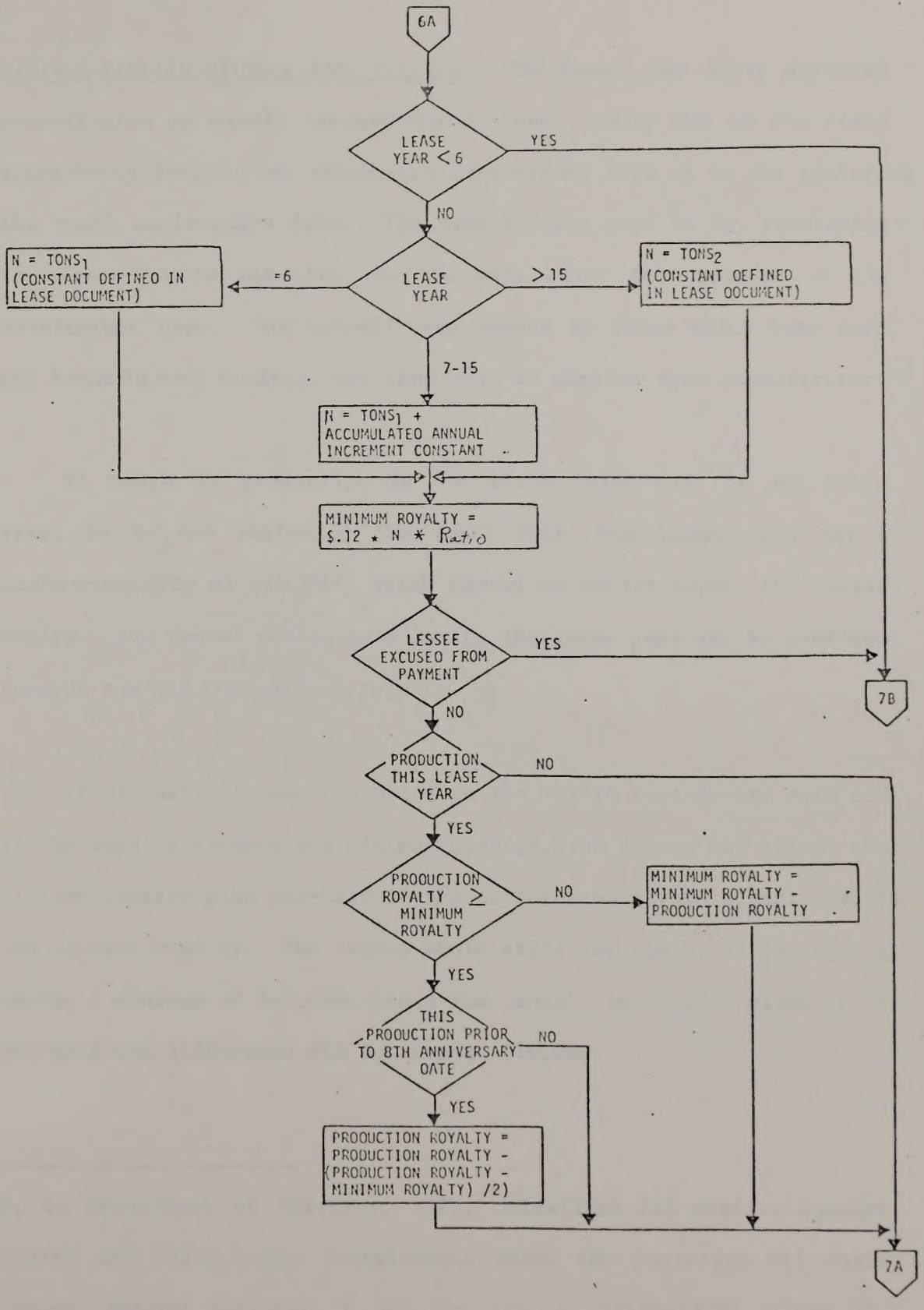


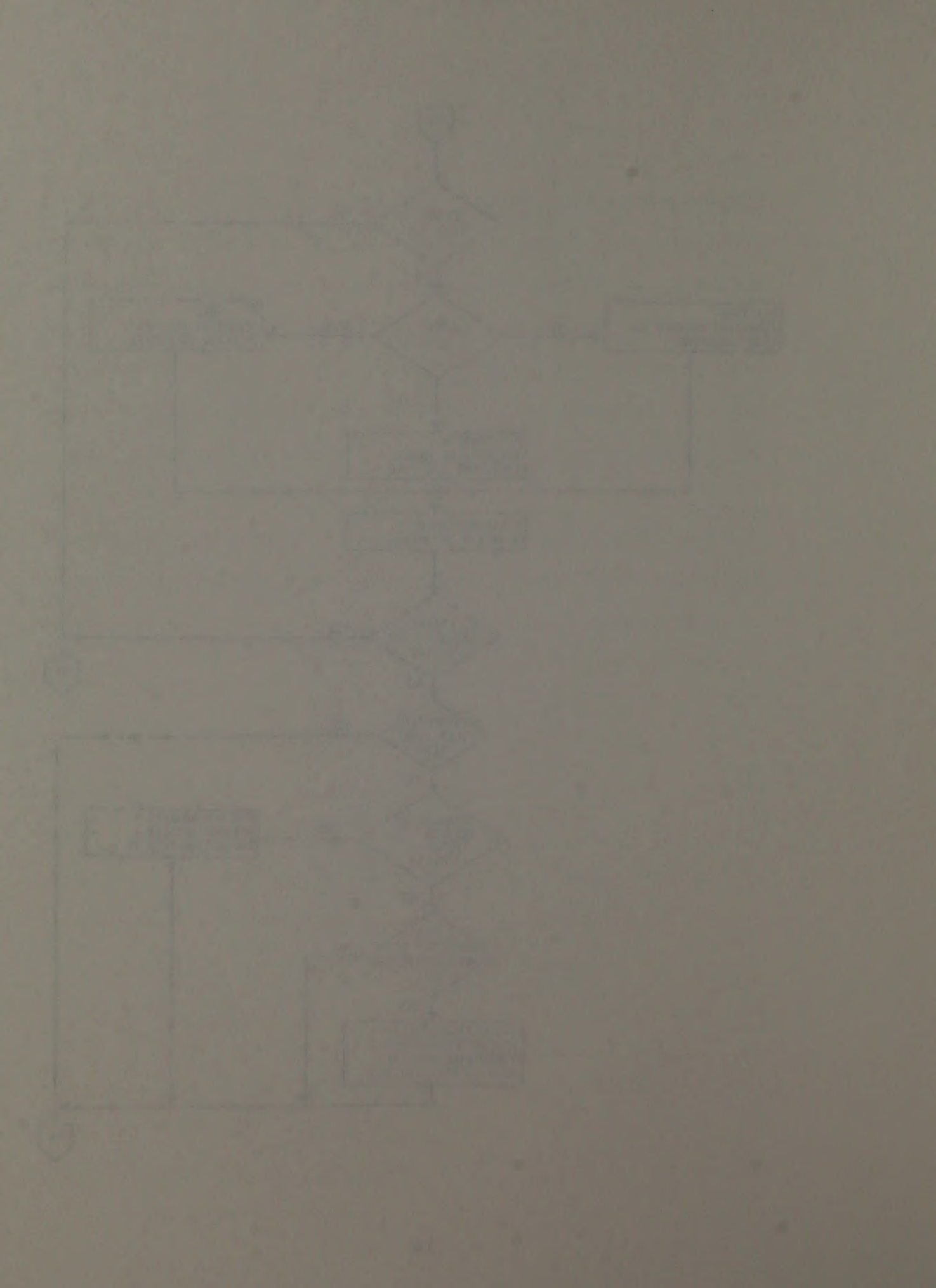
Minimum Royalty Sec. 7(e)(1). The lease shall pay a minimum royalty beginning at the end of the sixth lease year at the rate specified in the Lease, as adjusted by the price index factor [subsection (a)(1)(i)]. Thereafter, until the fifteenth year, the minimum royalty increases annually by the rate specified in the Lease and is adjusted by the price index factor. For the fifteenth year and each subsequent year, the minimum royalty will be adjusted only by the price index factor.

The minimum royalty may be waived if it can be shown that the lessee is prevented from implementing the development plan.

Sec. 7(e)(1) For the sixth and each succeeding Lease Year the Lessee shall pay a minimum royalty which, to the extent that royalties on production during that Lease Year in that amount have not been previously paid, shall be due and payable on the Anniversary Date at the end of that Lease Year. For the sixth Lease Year, the Lessee's minimum royalty shall be equal to the royalty due on shale oil under subsection (a)(1)(i) of this section on an annual production rate of ——— Tons of Oil Shale containing ——— gallons of shale oil per Ton of Oil Shale. The annual production rate for computing minimum royalty for each subsequent Lease Year up to and including the fifteenth Lease Year shall increase in an amount of ——— Tons of Oil Shale per year for each subsequent Lease Year; for the fifteenth and each subsequent Lease Year the annual rate shall be ——— Tons of Oil Shale. The Secretary may excuse the Lessee from compliance, in whole or in part, with the requirements of this paragraph (1) of subsection (e) during any year in which the Lessee is prevented by circumstances over which he has no control from implementing a development plan submitted under Section 10 of this lease.




6A
LEASE YEAR < 6
YES
NO
N = TONS1 (CONSTANT DEFINED IN LEASE DOCUMENT)
=6
LEASE YEAR
>15
N = TONS2 (CONSTANT DEFINED IN LEASE DOCUMENT)
7-15
N = TONS1 + ACCUMULATED ANNUAL INCREMENT CONSTANT
MINIMUM ROYALTY = $.12 * N * Ratio
LESSEE EXCUSED FROM PAYMENT
YES
7B
NO
PRODUCTION THIS LEASE YEAR
NO
YES
PRODUCTION ROYALTY ≥ MINIMUM ROYALTY
NO
MINIMUM ROYALTY = MINIMUM ROYALTY - PRODUCTION ROYALTY
YES
THIS PRODUCTION PRIOR TO 8TH ANNIVERSARY DATE
NO
YES
PRODUCTION ROYALTY = PRODUCTION ROYALTY - (PRODUCTION ROYALTY - MINIMUM ROYALTY) /2)
7A



Minimum Royalty Offsets Sec. 7(e)(2). The lessee may apply approved expenditures as credit against any minimum royalty due on the sixth anniversary date or any subsequent anniversary date up to and including the tenth anniversary date. The expenditures must be for developing the lease tracts and they must be made after the approval of the development plan. The expenditures cannot be those which were used for Bonus Offset Credits, but they must be similar type expenditures.[7/]

If there is production in the sixth lease year or any other year, up to and including the tenth year, the lessee must pay a minimum royalty of $10,000, which cannot be offset except for rental monies. Any rental monies paid during the lease year may be credited towards the $10,000 minimum royalty.

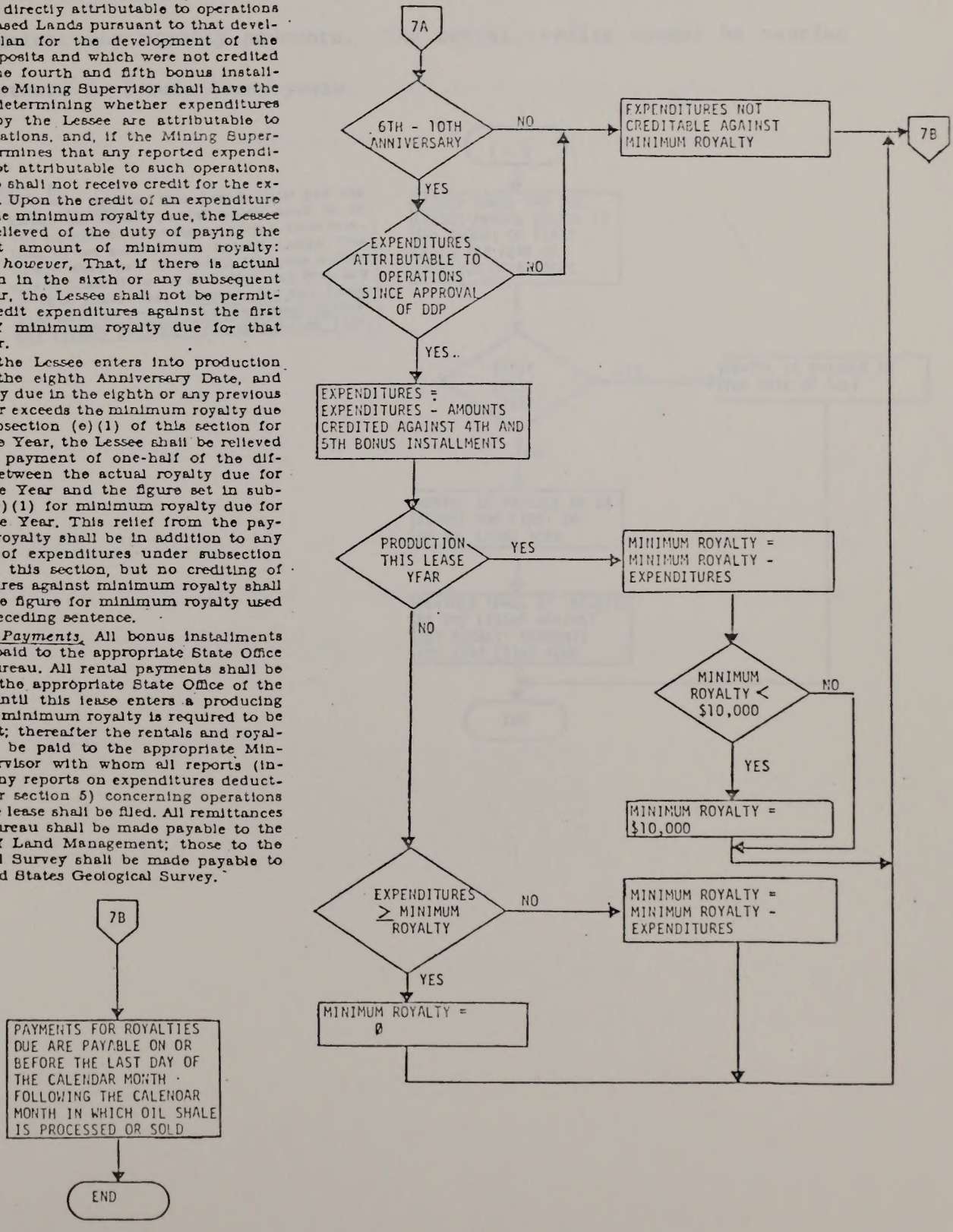
If production commences prior to the eighth anniversary date and if the royalty exceeds the minimum royalty, the lessee may offset the minimum royalty plus one-half of the difference between actual royalty and minimum royalty. The lessee would still pay the U. S. Geological Survey a minimum of $10,000, minus the rental, in royalty payments if one-half the difference did not exceed $10,000.

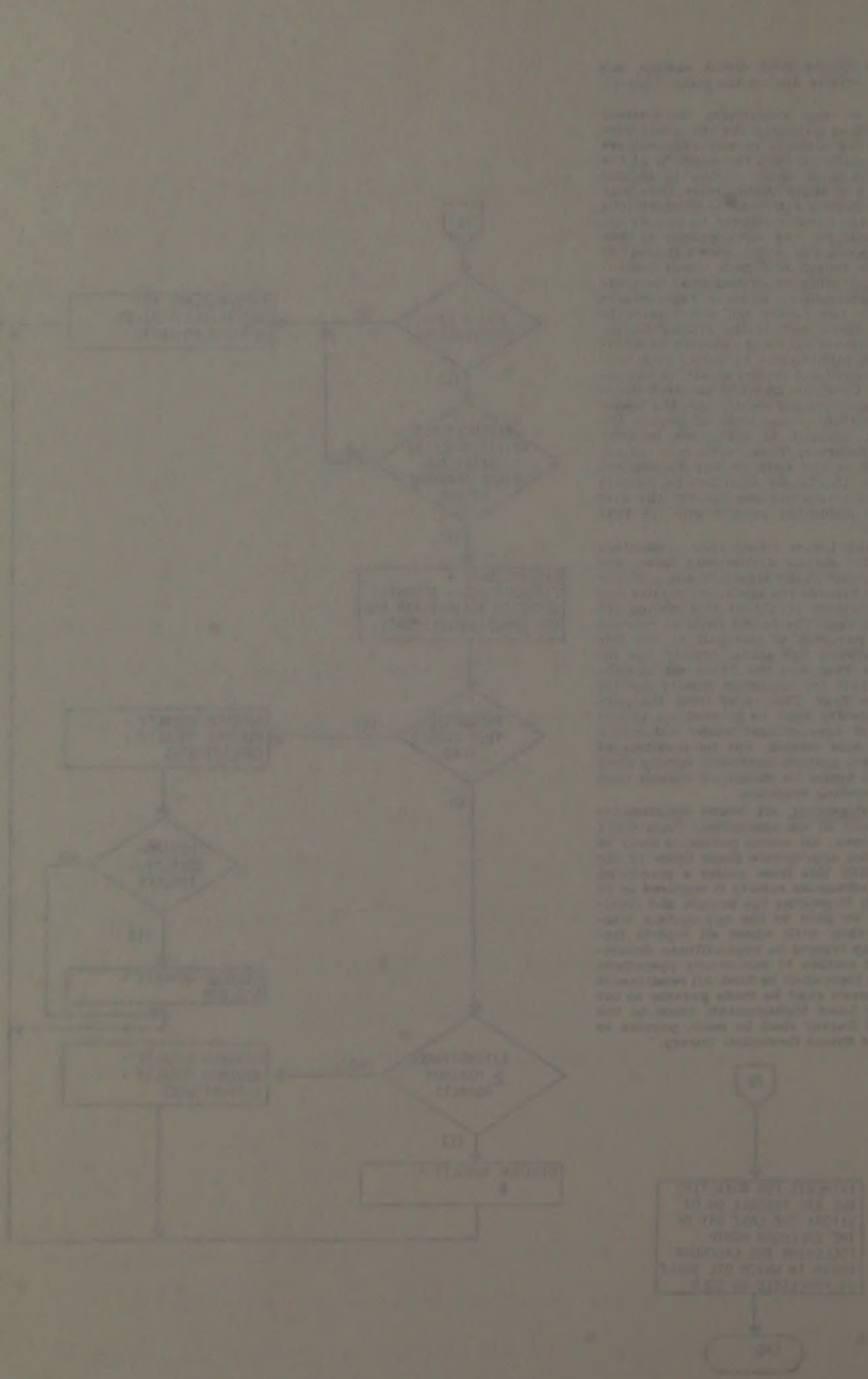
7/ U. S. Department of Interior, 1975, Guidelines for credits against fourth and fifth bonus installments under the prototype oil shale leases, Federal Register, V. 40, No. 125, p. 27281-27283. (June 27, 1975)

Sec. 7(e)(2). The Lessee may credit against any minimum royalty due on the sixth Anniversary Date or any subsequent Anniversary Date up to and including the tenth Anniversary Date the amount of any expenditures which are made between the approval of the development plan under section 10 of this lease and the tenth Anniversary Date and which are directly attributable to operations on the Leased Lands pursuant to that development plan for the development of the Leased Deposits and which were not credited against the fourth and fifth bonus installments. The Mining Supervisor shall have the duty of determining whether expenditures credited by the Lessee are attributable to such operations, and, if the Mining Supervisor determines that any reported expenditure is not attributable to such operations, the Lessee shall not receive credit for the expenditure. Upon the credit of an expenditure against the minimum royalty due, the Lessee will be relieved of the duty of paying the equivalent amount of minimum royalty: *Provided, however,* That, if there is actual production in the sixth or any subsequent Lease Year, the Lessee shall not be permitted to credit expenditures against the first $10,000 of minimum royalty due for that Lease Year.

(f) If the Lessee enters into production prior to the eighth Anniversary Date, and the royalty due in the eighth or any previous Lease Year exceeds the minimum royalty due under subsection (e)(1) of this section for that Lease Year, the Lessee shall be relieved from the payment of one-half of the difference between the actual royalty due for that Lease Year and the figure set in subsection (e)(1) for minimum royalty due for that Lease Year. This relief from the payment of royalty shall be in addition to any crediting of expenditures under subsection (e)(2) of this section, but no crediting of expenditures against minimum royalty shall reduce the figure for minimum royalty used in the preceding sentence.

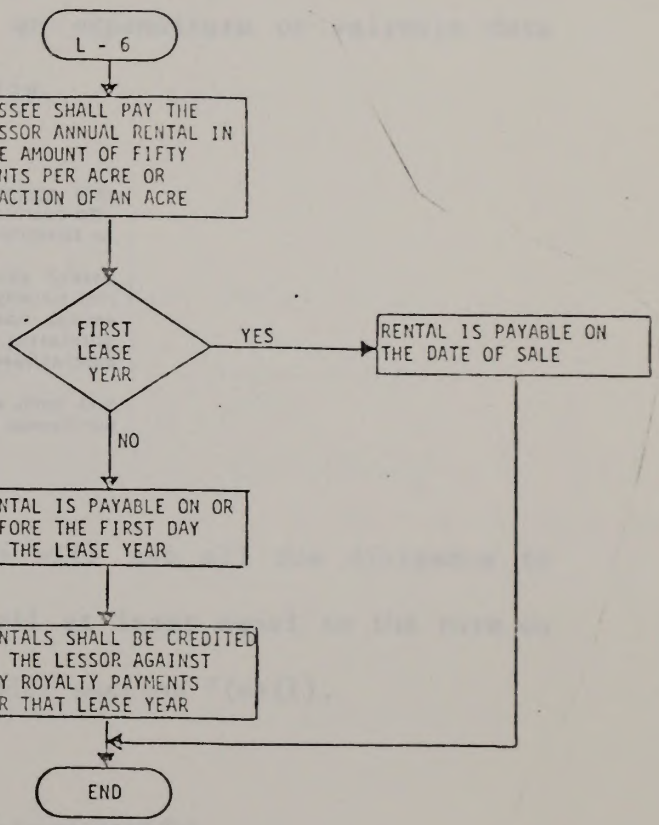
Sec. 8. *Payments.* All bonus installments shall be paid to the appropriate State Office of the Bureau. All rental payments shall be made to the appropriate State Office of the Bureau until this lease enters a producing status or minimum royalty is required to be paid on it; thereafter the rentals and royalties shall be paid to the appropriate Mining Supervisor with whom all reports (including any reports on expenditures deductible under section 5) concerning operations under the lease shall be filed. All remittances to the Bureau shall be made payable to the Bureau of Land Management; those to the Geological Survey shall be made payable to the United States Geological Survey.

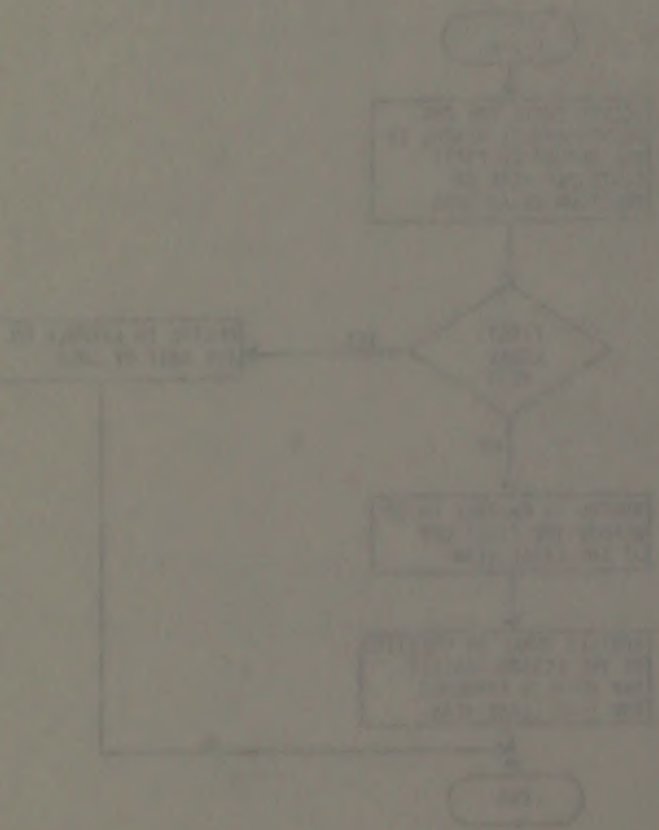

7A
6TH - 10TH ANNIVERSARY
NO
EXPENDITURES NOT CREDITABLE AGAINST MINIMUM ROYALTY
7B
YES
EXPENDITURES ATTRIBUTABLE TO OPERATIONS SINCE APPROVAL OF DDP
NO
YES
EXPENDITURES = EXPENDITURES - AMOUNTS CREDITED AGAINST 4TH AND 5TH BONUS INSTALLMENTS
PRODUCTION THIS LEASE YEAR
YES
MINIMUM ROYALTY = MINIMUM ROYALTY - EXPENDITURES
NO
MINIMUM ROYALTY < $10,000
NO
YES
MINIMUM ROYALTY = $10,000
EXPENDITURES ≥ MINIMUM ROYALTY
NO
MINIMUM ROYALTY = MINIMUM ROYALTY - EXPENDITURES
YES
MINIMUM ROYALTY = 0
7B
PAYMENTS FOR ROYALTIES DUE ARE PAYABLE ON OR BEFORE THE LAST DAY OF THE CALENDAR MONTH FOLLOWING THE CALENDAR MONTH IN WHICH OIL SHALE IS PROCESSED OR SOLD
END



As stated in Section 6 of the lease, the rental shall be credited against any royalty payments. The rental credits cannot be carried forward to future lease years.

Sec. 6. *Rentals.* The Lessee shall pay the Lessor an annual rental which shall be in the amount of 50 cents for each acre or fraction of an acre of the Leased Lands. The Lessee shall pay the rental for each subsequent Lease Year on or before the first day of that Lease Year. Rentals for any Lease Year shall be credited by the Lessor against any royalty payments for that Lease Year.


L - 6
LESSEE SHALL PAY THE LESSOR ANNUAL RENTAL IN THE AMOUNT OF FIFTY CENTS PER ACRE OR FRACTION OF AN ACRE
FIRST LEASE YEAR
YES
RENTAL IS PAYABLE ON THE DATE OF SALE
NO
RENTAL IS PAYABLE ON OR BEFORE THE FIRST DAY OF THE LEASE YEAR
RENTALS SHALL BE CREDITED BY THE LESSOR AGAINST ANY ROYALTY PAYMENTS FOR THAT LEASE YEAR
END



Audits and Inspections. Section 15 of the lease and Title 30 CFR, Parts 231.62 and 231.70 provide the Mining Supervisor with authority to conduct audits, inspections, and investigations whenever needed to substantiate the creditability of an expenditure or validate data that was used to calculate the royalty.

Sec. 15. *Inspection and investigation.* The Lessee shall permit any duly authorized officer or representative of the Department at any reasonable time:
(a) to inspect or investigate the Leased Lands and all surface and underground improvements, works, machinery, and equipment, and all books and records pertaining to operations and surveys or investigations under this lease; and
(b) to copy and make extracts from any books and records pertaining to operations under this lease.

Diligence Requirements. The lessee will use all due diligence to attain a production rate of shale oil at least equal to the rate on which minimum royalty is computed under section 7(e)(1).

Sect. 10.(a)(3) a requirement that the Lessee use all due diligence in the orderly development of the Leased Deposits, and, in particular, to attain, at as early a time as is consistent with compliance with all the provisions of this lease, production at a rate at least equal to the rate on which minimum royalty is computed under section 7(e)(1).

ROYALTY CALCULATIONS

The method of computing the royalty depends on whether the oil shale is extracted by mining methods or processed by in-situ methods. Items 1 and 2 illustrate the calculations of computing the royalty.

1. Royalty from in situ process, dollars:

$$\text{Royalty} = \text{Gross heat of combusion of all products (btu's)} \times \frac{1 \text{ gallon oil}}{152{,}700 \text{ btus}} \left| \frac{1 \text{ ton oil shale}}{30 \text{ gals oil}} \right| \frac{\$0.12}{\text{ton}} \left| \text{ index factor} \right.$$

$$= \frac{\text{Gross heat of combustion (btus)}}{38{,}175{,}000} \left| \text{ index factor} \right.$$

2. Royalty from mining when processed or sold, dollars:

   a. Average modified Fischer assay $\leq$ 30 gals/ton

$$\text{Royalty} = \text{tons mined} \left| \frac{\$0.12 - (\$0.01(30-\text{assay}))}{\text{ton}} \right| \text{index factor}$$

   b. Average modified Fischer assay $>$ 30 gals/ton

$$\text{Royalty} = \text{tons mined} \left| \frac{\$0.12 + (\$0.01(\text{assay} - 30))}{\text{ton}} \right| \text{index factor}$$

   c. If $\$0.12 - (\$0.01(30-\text{assay})) < \$0.04$

   Then:

$$\text{Royalty} = \text{tons mined} \left| \frac{\$0.04}{\text{ton}} \right| \text{index factor}$$

In order to determine the royalty due the government, the lessee must submit a monthly data sheet. All data must be backed up with books showing lab analysis, daily data sheets with operational data, to be kept by lessee, and should be available on request.

Table 1 illustrates an example of the data needed for royalty calculation of a 50,000 barrel-per-day in situ operation or a 50,000 barrel-per-day mining operation. Standard forms will be sent to the lessees by the Geological Survey. These forms will be filled out by the lessee and sent to the appropriate Geological Survey office once a month with the royalty payments.

Basis = 50,000 barrels/day of shale oil by modified in situ methods

and

50,000 barrels/day of shale oil by underground mining

and aboveground retorting.

TABLE 1. -- Data needed for oil shale royalty calculations

(for demonstration use only)

Time of operation	August 1, 1986 thru August 30, 1986
Oil shale produced, tons (surface retort only)	2,268,784
Fischer assay of oil shale, gals/ton	27
Price adjustment index factor	1.226
Gas product, mmscf (MIS only)	40,342
Gas heat of combustion, btu's/scf (MIS only)	78.14
Shale oil produced (MIS only)	1,458,500
Oil heat of combustion, btu's/gal (MIS only)	135,298

In Situ Retorting

$$\text{Royalty} = \frac{\text{Gross heat of combustion}}{1} \left| \frac{1 \text{ gallon oil}}{152{,}700 \text{ btu's}} \right.$$

$$\times \frac{1 \text{ ton oil shale}}{30 \text{ gallons oil}} \left| \frac{0.12}{\text{ton}} \right| \text{Index factor}$$

$$\text{Royalty} = \$ \frac{\text{Gross heat of combustion (btu's)}}{38{,}175{,}000} \left| \text{Index factor} \right.$$

$$\text{Gross heat of combustion from oil} = \frac{50{,}000 \text{ bbls}}{\text{day}} \left| \frac{42 \text{ gal}}{1 \text{ bbl}} \right| \frac{135{,}298 \text{ btu's}}{1 \text{ gal}}$$

$$= (2.84)(10)^{11} \text{ btu's/day}$$

$$\text{Gross heat of combustion from gas} = \frac{40.342 \text{ mmscf}}{} \left| \frac{78.14 \text{ btu's}}{\text{scf}} \right| \frac{}{29.17 \text{ days}}$$

$$= (1.08)(10)^{11} \text{ btu's/day}$$

$$\text{Total gross heat of combustion} = (2.84)(10)^{11} \text{ btu's/day}$$

$$+ (1.08)(10)^{11} \text{ btu's/day}$$

$$\text{Total gross heat of combustion} = (3.92)(10)^{11} \text{ btu's/day}$$

Index factor for 1977 = 1.226

$$\text{Royalty} = \frac{(3.92)(10)^{11} \text{ btu's}}{\text{day}} \left| \frac{1.226}{38{,}175{,}000} \right.$$

$$= \$ \, 12{,}589/\text{day}$$

$$= \underline{\$4{,}406{,}213/\text{year}}$$

$$= \$367{,}184/\text{month}$$

$$= \underline{\$0.1052/\text{ton oil shale retorted}}$$

Aboveground Retorting

$$\text{Royalty} = \frac{\text{Tons retorted}}{} \left| \frac{\$0.12-(\$0.01)(30-\text{Assay})}{\text{ton}} \right| \text{Index factor}$$

$$= \frac{77{,}778 \text{ tons}}{\text{day}} \left| \frac{0.12 - \$0.01(30-27)}{\text{ton}} \right| 1.226$$

$$= \$8{,}582/\text{day}$$

$$= \underline{\$3{,}003{,}708/\text{year}}$$

$$= \$250{,}309/\text{month}$$

$$= \underline{\$0.1103/\text{ton oil shale retorted}}$$

Mineral Royalty

There shall be a royalty calculated on all minerals other than shale oil which are processed or sold. The royalty shall be based on the value of the minerals at the point of shipment. In case alumina and soda ash are made from dawsonite and sold, examples of how the royalties are to be calculated are given. For easy calculation, 100 tons per day of alumina and soda ash are used.

Alumina

First 10 lease years	=	$\frac{100 \text{ tons}}{\text{day}} \mid \frac{\$160}{\text{ton}}$[8/] $\mid 0.03$
	=	$480/day
	=	0.0040/ton oil shale
11th through 15th lease years	=	$16,000/day (0.04)
	=	$640/day
	=	$0.0053/ton oil shale
16th year until end of lease	=	$16,000/day (0.05)
	=	$800/day
	=	$0.0067/ton oil shale

8/ Farris, Clifford B. and Mains, Charles J., 1978, Dawsonite and Nahcolite Survey: DOE contract No. EC-77-s-07-1183, IDO-1683-1 (v. 1 of 2), p. A-56. (April 1978)

Soda Ash

First 10 lease years = $\frac{100 \text{ tons}}{\text{day}} \mid \frac{\$55}{\text{ton}}[9] \mid 0.03$

= $165/day

= $0.0014/ton oil shale

11th through 15th = ($5,500/day) 0.04

= $220/day

= $0.0018/ton oil shale

16th year until end of lease = ($5,500/day) 0.05

= $275/day

= $0.0023/ton oil shale

9/ Ibid.

MINIMUM ROYALTY

In order to encourage the lessees to reach production as fast as possible, Section 7(e)(1) of the Prototype Oil Shale Lease requires the lessee to pay a minimum royalty rate of production. Table 4 gives the minimum production rates for Tracts C-a and C-b which are specified in the individual leases. Therefore as the lease states that the minimum royalty will be based on 30 gallons per ton oil shale, no adjustment for grade is required or necessary. The royalty rate index factor is based on the average price of oil at the wellhead reported for the states of Colorado, Wyoming, and Utah [Sec. 7(a)(1)]. If the data that are used for calculating the index factor are not received in time, the last known index factor will be used, and at such time the index factor does become known, there will be a correction made for the minimum royalty. The same is true for the actual royalty if there is production.

Table 5 gives the index factor for 1970 through 1977. The index factor for 1974 is 1.000, as 1974 is the year that the leases were leased. The data for calculating the index factors will be sent to the lessees by the Geological Survey as soon as the data reports are published. Since minimum royalties are due at the end of the lease year, the index factor should be known before the minimum royalty is due.

TABLE 2. -- Minimum production and royalty rates for oil shale tracts C-a and C-b

Lease Year and Due Date	Production Rate tons/year	Royalty $/year
		10/
Tract Ca - 6th (March 1, 1981)	1,130,000	$135,600X(1980 I.F.)
Tract Cb - 6th (April 1, 1981)	616,000	73,920X(1980 I.F.)
Tract Ca - 7th (March 1, 1982)	2,260,000	$271,200X(1981 I.F.)
Tract Cb - 7th (April 1, 1982)	1,232,000	147,840X(1981 I.F.)
Tract Ca - 8th (March 1, 1983)	3,390,000	$406,800X(1982 I.F.)
Tract Cb - 8th (April 1, 1983)	1,848,000	221,760X(1982 I.F.)
Tract Ca - 9th (March 1, 1984)	4,520,000	$542,400X(1983 I.F.)
Tract Cb - 9th (April 1, 1984)	2,464,000	295,680X(1983 I.F.)
Tract Ca - 10th (March 1, 1985)	5,650,000	$678,000X(1984 I.F.)
Tract Cb - 10th (April 1, 1985)	3,080,000	369,600X(1984 I.F.)
Tract Ca - 11th (March 1, 1986)	6,780,000	$813,600X(1985 I.F.)
Tract Cb - 11th (April 1, 1986)	3,696,000	443,520X(1985 I.F.)
Tract Ca - 12th (March 1, 1987)	7,910,000	$949,200X(1986 I.F.)
Tract Cb - 12th (April 1, 1987)	4,312,000	517,440X(1986 I.F.)
Tract Ca - 13th (March 1, 1988)	9,040,000	$1,084,800X(1987 I.F.)
Tract Cb - 13th (April 1, 1988)	4,928,000	591,360X(1987 I.F.)
Tract Ca - 14th (March 1, 1989)	10,170,000	$1,220,400X(1988 I.F.)
Tract Cb - 14th (April 1, 1989)	5,544,000	665,280X(1988 I.F.)
Tract Ca - 15th (March 1, 1990)	11,300,000	$1,356,000X(1989 I.F.)
Tract Cb - 15th (April 1, 1990)	6,160,000	739,200X(1989 I.F.)
Tract Ca - 16th to end of lease	11,300,000	$1,356,000X(I.F.)
Tract Cb - 16th to end of lease	6,160,000	739,200X(I.F.)

10/ Crude Petroleum, Petroleum Products, and Natural Gas Liquids: (Final Summary), Energy Data Reports, DOE, EIA, Washington, D.C. 20467.

(See following table for calculation of index factor as required by Sec. 7(a)(1)(i)B of the Lease.)

TABLE 3. -- Index factor ratio used to calculate the royalty rates for tracts C-a and C-b[11/]

Year	COLORADO			UTAH			WYOMING			3 STATE TOTAL			Index Factor
	Quantity k-bbls	Wellhead Value k-$	Value $/bbl	Quantity k-bbls	Wellhead Value k-$	Value $/bbl	Quantity k-bbls	Wellhead Value k-$	Value $/bbl	Quantity k-bbls	Wellhead Value k-$	Value $/bbl	
1970	24,723	78,619	3.18	23,370	65,603	2.81	160,345	469,811	2.93	208,438	614,033	2.95	0.432
1971	27,391	92,855	3.39	23,630	71,866	3.04	148,114	459,079	3.10	199,135	623,800	3.13	0.459
1972	32,015	109,171	3.41	26,570	80,773	3.04	140,011	432,071	3.09	198,596	622,015	3.13	0.459
1973	36,590	155,507	4.25	32,656	117,743	3.61	141,914	541,820	3.82	211,160	815,070	3.86	0.566
1/ 1974	37,508	283,904	7.57	39,363	279,858	7.11	139,997	914,360	6.53	216,868	1,478,122	6.82	1.000
1975	38,089	365,654	9.60	42,301	348,131	8.23	135,943	983,705	7.24	216,333	1,697,570	7.85	1.151
1976	38,992	376,273	9.65	34,304	318,911	9.30	134,149	971,235	7.24	207,445	1,666,419	8.03	1.177
1977	39,460	398,457	10.10	33,113	308,872	9.33	136,472	1,039,948	7.62	209,045	1,747,277	8.36	1.226
1978	36,797	365,024	9.92	31,368	313,009	9.98	137,385	1,258,293	9.16	205,550	1,936,326	9.42	1.381
1979													
1980													

1/ Calendar year lease was signed is considered the base year.

11/ Ibid

ROYALTY OFFSET CREDITS

As an incentive for diligent development of the leased lands, the lease allowed credits for any expenditures prior to the third and fourth anniversary dates which were directly attributable to operations for the development of the leased deposits against the fourth and fifth bonus installments of the five installment bonus bids of the lease tracts. Likewise, the lease allows the minimum royalty due the government for the sixth through the tenth lease years to be offset with expenditures which are directly attributable to operations for the development of the lease deposits.

When production does commence, a minimum royalty of $10,000 per year must be paid the Geological Survey. The following depicts the equations used for calculating the royalty offsets:

1. Rentals paid at the beginning of each lease may be used as a credit towards any royalty due that year, but cannot be carried forward as a credit for future lease years.

2. Lease years 6, 7 and 8.

$$\text{Royalty offsets} = \text{Minimum royalty} + \tfrac{1}{2}(\text{Royalty}^{12/} - \text{Minimum}) - (\$10{,}000 - \text{Rental})^{13/}$$

3. Lease years 9 and 10.

$$\text{Royalty offsets} = \text{Minimum royalty (Index factor)} - (\$10{,}000 - \text{Rental})^{13/}$$

12/ Royalty must exceed minimum royalty for this part of the equation to be used.

13/ Any rent monies may be credited towards the minimum $10,000 royalty. If production did not occur during the year, rental monies may be applied towards the royalty offsets.

4. Lease year 11 until end of the lease - Extraordinary environmental costs and rentals paid are the only offset items that can offset royalty payments.

Tract C-a

6th year = $135,600)(1979 Index factor)

+ ½(Royalty - $135,600(1979 Index factor)) - ($10,000-Rental)

7th year = $271,200(1980 Index factor)

+ ½(Royalty - $271,200(Index factor)) - ($10,000-Rental)

8th year = $406,800(1981 Index factor)

+ ½(Royalty - $406,800(Index factor)) - ($10,000-Rental)

9th year = $542,400(1982 Index factor) - ($10,000-Rental)

10th year = $678,000(1983 Index factor) - ($10,000-Rental)

11th - 20th year = Royalty cannot be offset

Tract C-b

6th year = Minimum Royalty +½(Royalty - Minimum) - ($10,000-Rental)

= $73,920(1979 Index factor)

+ ½(Royalty - $73,920(1979 Index factor)) - ($10,000-Rental)

7th year = ($147,840)(1980 Index factor)

+ ½(Royalty - $147,840(1981 Index factor)) - ($10,000-Rental)

8th year = $221,760(1981 Index factor)

+ ½(Royalty - $221,760(1981 Index factor)) - ($10,000-Rental)

9th year = $295,680(1982 Index factor) - ($10,000-Rental)

10th year = $369,600(1983 Index factor) - ($10,000-Rental)

11th - 20th year = Royalty cannot be offset.

Section 6 of the lease allows credits of any rent monies towards royalty payments for that lease year.

1. C-a - Rental = $\frac{(5{,}089.70 \text{ acres})(\$0.50)}{(\text{acre})(\text{year})}$

= $\underline{\$2{,}545/\text{year}}$

2. C-b - Rental = $\frac{(5{,}093.90 \text{ acres})(\$0.50)}{(\text{acre})(\text{year})}$

= $\underline{\$2{,}547/\text{year}}$

The royalty offset expenditures will be handled in the same manner as bonus offset expenditures for the fourth and fifth bonus installments. All requests must be accompanied by evidence supporting that an actual expenditure has been incurred by the lessee. Evidence of payment shall be submitted with a brief, but accurate description of the expenditure and its use.

SUMMARY AND CONCLUSIONS

The method of calculating royalty depends on whether the oil shale is extracted by mining methods or processed by in-situ methods. The lessee is required to keep books showing lab analyses and daily data sheets with operational data to backup the royalty data. Royalty monies due the government must be submitted to the U. S. Geological Survey once a month by the lessee using standard Geological Survey forms. The royalty rate adjustment index factor used will be the latest one published. Corrections to the rate adjustment will be done on a yearly basis.

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APPENDIX I

METHOD OF ASSAYING OIL FROM OIL SHALE USING THE FISCHER ASSAY PROCEDURE

Standard Method of Test for

OIL FROM OIL SHALE

(RESOURCE EVALUATION BY THE USBM FISCHER ASSAY PROCEDURE)

May 1980

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ASTM Designation D: 3904 79T

Standard Method of Test for

OIL FROM OIL SHALE (RESOURCE EVALUATION BY THE USBM FISCHER ASSAY PROCEDURE)

1. Scope

1.1 The method covers the determination of the amount of oil, water, and spent shale obtained upon prescribed heating of a representative oil shale sample that has been crushed to an appropriate size (2.36mm or 8 mesh). The amount of gas evolved can be calculated from data obtained in this procedure. This method is applicable to oil shale, which upon heating evolves liquid and gaseous products (Note 1). It has been tested over the range 19 - 227 liters per tonne (5 - 60 gallons per ton) of oil.

Note 1---The method does not include procedures for identifying the nature of the gas.

1.2 The method provides standardized data useful for oil shale resource evaluation. The method neither yields quantities that necessarily duplicate yields in experimental or commercial oil shale processes nor does it yield products that necessarily duplicate in physical or chemical nature the products that may be obtained in such experimental or commercial processes.

2. Applicable Documents

2.1 ASTM Standards (Note 2):

D 346 Standard Method of Collection and Preparation of Coke

Samples for Laboratory Analysis

D 1250 Standard Petroleum Measurement Tables

D 1796 Standard Method of Test for Water and Sediment in Crude Oils and Fuel Oils by Centrifuge

D 2013 Standard Method of Preparing Coal Samples for Analysis

E 11 Standard Specification for Wire-Cloth Sieves for Testing Purposes

Note 2---These methods may be found in Parts 18, 24, 25, and 26 of the 1977 Annual Book of ASTM Standards (Petroleum Products and Lubricants)

2.2 U.S. Bureau of Mines Publications

RI 3977 Method of Assaying Oil Shale by a Modified Fischer Retort by Stanfield, K.E. and Frost, I.C., U.S. BuMines Rept. of Inv. 3977, 1946, 11 pp.

RI 4477 Method of Assaying Oil Shale by a Modified Fischer Retort (Revision of RI 3977) by Stanfield, K.E. and Frost, I.C., U.S. BuMines Rept. of Inv. 4477, 1949, 13 pp.

RI 6676 Automated Modified Fischer Retorts for Assaying Oil Shale and Bituminous Materials by Hubbard, A.B., U.S. BuMines Rept. of Inv. 6676, 1965, 19 pp.

2.3 Other Publications

2.3.1 Taggart, A.F., "Handbook of Mineral Dressing - Ores and Industrial Minerals", John Wiley and Sons, Inc., 1956, Table 13, Section 19

2.3.2 Heistand, Robert N., "The Fischer Assay: Standard for the Oil Shale Industry", Energy Sources, vol. 2, No. 4, 1976, pp 397-405.

2.3.3 Smith, John Ward, "Stratigraphic Change in Organic

Composition Demonstrated by Oil Specific Gravity-Depth Correlation in Tertiary Green River Oil Shales, Colorado, Am. Assoc. Petrol. Geol., v. 47, No. 5, May 1963, pp 804-813.

3. Summary of Method

3.1 Crushed raw shale is sampled by riffle-splitting. The determination of the amount of oil available from oil shale is made by heating the raw shale from ambient temperature to 500°C in cast aluminum alloy retorts. The vapors distilled from the sample are cooled and the condensed fraction is collected. The oil and water fractions are separated, the water volume (converted to weight equivalent) is measured and subtracted from the oil plus water weight. The weight of uncondensable gases evolved (gas-plus-loss) is then calculated by difference.

4. Significance and Use

4.1 This method is useful as a basis of comparing the oil-producing capabilities of oil shales.

4.2 Because the U.S. Department of Energy, Laramie Energy Technology Center (formerly a U.S. Bureau of Mines Laboratory) has developed an extensive record of data concerning the properties of oil shales from various regions by the use of this method, the method provides a means of comparing oil shale deposits.

4.3 The extensive use of the procedure makes it a basis for standardizing other evaluation methods for oil shale.

5. Terminology

5.1 Oil Shale - a sedimentary rock containing insoluble organic matter which upon heating yields an oil similar to petroleum.

5.2 Shale Oil - the organic liquid obtained from the retort-

ing of oil shale.

5.3 Assay - the determination of the potential yield of a specific component from a resource material.

5.4 Gas-plus-loss - a term covering evolved gases not condensed at 0°±3°C plus experimental error. In addition to experimental error, gas-plus-loss values arise from organic material and from minerals present in the oil shale which may release hydrogen sulfide (H_2S) or carbon dioxide (CO_2). An example of these minerals are: Dolomite ($CaMg(CO_3)_2$) and Pyrite (FeS_2).

5.5 Resource Evaluation - evaluation of an oil shale resource is the determination of the approximate oil resource present in the deposit. Oil yield assay results combined with stratigraphic and geographic distribution permit estimation of a shale oil resource.

6. Interferences

6.1 An erroneously high gas-plus-loss value will be obtained if the system is not gas tight. If smoke or vapor is detected rising from the system, or a pungent odor is present, a leak is evident and the sample must be re-run.

7. Apparatus

7.1 Assay Bench[1] consisting of the components (Figure 1):

Temperature Control Unit[2] (Figure 1)

Cooling Bath capable of holding a constant temperature through condensers of 0°±3°C (Figures 1, 2, and 8)

Constant Temperature Bath capable of maintaining 40°±5°C

Electric Heater (Figures 6 and 7)

Programmer[2] (Figure 1)

Recorder (Figure 1)

and many calcium compounds are used medicinally. (Dangerous Properties of Industrial Materials by N.I. Sax, pp 509).

Note 5---CAUTION, harmful if inhaled -- high concentrations may cause unconsciousness or death. Avoid prolonged or repeated breathing of vapor. Use only with adequate ventilation. Do not take internally. Avoid prolonged or repeated contact with skin. Do not get in eyes. Do not store in open or unlabeled or mislabeled containers. Do not store degrease, clean-out sludge in tightly sealed containers. Store containers out-of-doors away from combustible materials. Do not use cutting or welding torches, open flames, electric arcs or glowing surface on empty or full drums that contain trichloroethylene (methylene chloride).

Note 6---CAUTION, Danger, extremely flammable. Vapors may cause flash fire. Keep away from heat, sparks, and open flame. Keep container closed. Use with adequate ventilation. Vapors may spread long distances and ignite explosively. Avoid build-up of vapors and eliminate all sources of ignition, especially non-explosion proof electrical apparatus and heaters. Avoid prolonged breathing of vapor or spray mist. Avoid contact with eyes and skin. In case of spillage, absorb and flush with large volumes of water. In case of fire, use water, dry chemical, CO_2 or foam.

Note 7---Slight fire hazard when exposed to fire or flame. Moderate explosion hazard when exposed to flame. Slight irritant when exposed to skin. (Dangerous Properties of Industrial Materials by N.I. Sax, pp 737).

Note 8---See section on lead compounds in Dangerous Properties of Industrial Materials by N.I. Sax, pp 861.

9. Sampling

9.1 Sample size and sample preparation procedures should comply with ASTM D346-78, D2013-72, and E-11.

9.2 A minus 2.36mm particle size (8 mesh, U.S. Standard) (see E-11) should be used for better representation in this method.

9.3 Because of the non-homogeneous nature of oil shale, a 95±10g sample should be t[illegible]en by riffle-splitting only.

10. Preparation of Apparatus

10.1 All equipment should be cleaned and dried prior to each assay. Special attention should be given the distillate outlet of the retort, as it tends to accumulate shale dust,

carbonized material and oil.

10.2 The cooling medium temperature for the condensers and cooling bath should be maintained at 0°±3°C.

11. Procedure

11.1 Weigh the entire contents of a riffle-split (approximately 95±10g) in a tared retort. For best transmissivity of heat, aluminum discs (up to 5 are recommended) and a chimney, as shown in Figure 5, should be used separating the sample between each disc. Pouring the sample near or into the vent tube should be avoided (Note 9). Place cap into position and tap lightly to seal. Check that vent pipes are tight.

Note 9---The effects of dust vary according to the composition. If it is organic dust, it is primarily a nuisance, but may produce asthma by being an allergen. If the dust contains toxic compounds, either organic or inorganic, the hazard is that of the toxic component (Dangerous Properties of Industrial Materials by N.I. sax, pp 711). A dust mask is recommended.

11.2 Weigh a clean, dry receiver and adapter to the nearest 0.01g. Assemble the retort apparatus as shown in Figure 2.

11.3 Immerse the receiver to the 100ml mark in a cooling bath (Figure 2). The cooling medium circulating through the condensers and cooling bath must be maintained at 0°±3°C for all assays.

11.4 The system must be gas tight (See 6.1 and CAUTION, Note 10). Turn on the power switch, controls, timer, and recorder. Heat the sample according to the heating profile shown in Figure 9. The sample is heated in such a manner as to go from ambient (the starting point marked by letter "A", see Figure 9) to 500°±

5°C in 40 minutes. Maintain the 500°C temperature for a minimum of 40±5 minutes, concluding when the evolution of oil has been completed. This proper heating time and temperature must be observed to maintain uniform results. For oil yields greater than 60 gallons per ton, a longer maintenance time at 500°C may be necessary.

Note 10---CAUTION, the gases evolved during distillation may be toxic and should be vented to the outside atmosphere through a hydrogen sulfide (H_2S) scrubber such as a freshly prepared (10g/100ml) lead acetate solution ($Pb(C_2H_3O_2)_3H_2O$); as an example: high pyrite (FeS_2) bearing shales can produce hydrogen sulfide (H_2S).

11.5 After the program is completed, turn off all controls, disassemble the apparatus, remove the retort from the oven and add a calcium chloride ($CaCl_2$) drying tube to the distillate outlet (this precaution is necessary to avoid absorption of water on the spent shale in the retort). Allow the retort to return to ambient temperature.

11.6 After drying the outer surfaces, weigh receiver, adapter, and contents to the nearest 0.01g.

11.7 Separate the receiver and adapter. Immerse the receiver to the 100ml mark into the constant temperature bath until an equilibrium temperature of 40°±5°C has been attained.

11.8 The retorted oils must be free of water and be mixed thoroughly before relative density determinations are made. Centrifuge the warm receiver as described in ASTM D1796-68, read and record the volume of water, and take an aliquot of the oil fraction for oil relative density measurement (see 2.3.3 and Note 11).

Note 11---When there is insufficient oil for an accurate relative density measurement, the volume of oil is approximated

from its weight and an assumed median value for relative density of 0.920 is used. See Smith, J.W., Bull. Am. Assoc. Petrol. Geol., v. 47, No. 5, May 1963, pp 804-813.

11.9 The oil should be warmed to 37.8°C (100°F) to obtain sufficient fluidity. Determine the relative density of the oil using a pipet or pycnometer (a convenient size is approximately 1ml). Pipet volumes should be calibrated and relative densities must be reported at 15.6°C/15.6°C.

11.9.1 In order to express oil relative densities at a standard temperature (15.6°C (60°F)), the measured relative densities were corrected from 37.8°C/37.8°C (100°F) to 15.6°C/15.6°C (60°F) according to ASTM D1250-56. The shale oil density corrections are as follows:

Observed Relative Density	Correction
0.800 - 0.843	+0.010
0.844 - 0.916	+0.009
0.917 - 1.000	+0.008

12. Calculations

12.1 Milliliters of oil

$$\text{Ml oil} = \frac{(\text{gross wt. from 11.6}) - (\text{wt. from 11.2}) - (\text{ml water from 11.8})}{\text{relative density from 11.9.1}}$$

12.2 Milliliters of oil (or water) per gram of shale

$$\text{Ml of oil (or water) (see 11.8, Note 11)} = \frac{\text{ml of oil (or water) from 11.8}}{\text{weight of sample from 11.1}}$$

12.3 Oil yield, weight percent

$$\text{Oil, wt.\%} = \frac{(\text{gross wt. from 11.6}) - (\text{wt from 11.2}) - (\text{ml water from 11.8})}{\text{weight of sample from 11.1}} \times 100$$

12.4 Gas-plus-loss, weight percent

$$\text{Gas + loss wt.\%} = \frac{\text{(wt of sample from 11.1) - (wt of oil + water + spent shale)}}{\text{weight of sample from 11.1}} \times 1$$

12.5 Gallons of oil (or water) per ton of shale

$$\text{Gallons of oil (or water) (see 11.8, Note 11) per ton of shale} = \frac{\text{ml of oil (or water) from 11.8} \times 2.397}{\text{weight of sample from 11.1}} \times 100$$

12.6 Water yield, weight percent

$$\text{Water, wt.\%} = \frac{\text{ml water from 11.8}}{\text{wt of sample from 11.1}} \times 100$$

12.7 Spent shale

$$\text{\% Spent shale} = \frac{\text{wt of spent shale after retorting}}{\text{weight of sample from 11.1}} \times 100$$

13. Precision

13.1 These criteria were developed by a cooperative test program evaluated according to ASTM Manual on Determining Precision Data for ASTM Methods on Petroleum Products and Lubricants; Research Report No. RR D-2 - 1007.

13.2 Repeatability of oil - duplicate results by the same operator should be considered suspect if they differ by more than 4.2 liters/tonne (1.0 gallon/ton).

13.3 Reproducibility of oil - the results submitted by each of two laboratories should be considered suspect if they differ by more than 8.3 liters/tonne (2.0 gallons/ton).

13.4 The results of the cooperative test program, from which these values have been derived, are filed at ASTM Headquarters as Research Report No. RR _____; D-2

13.5 The American Society for Testing and Materials

takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in these standards. Users of these standards are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

FOOTNOTES

1. Can be purchased through Electric Power Equipment Company Commerce City, Colorado.
2. Can be purchased through the following: Gammaflux, Inc., Reston, Va. or Leeds and Northrup, Denver, Co.
3. Can be purchased through Kontes of California, San Leandro, California.
4. Can be purchased through Arapahoe Aluminum Foundry, Englewood, Colorado.
5. Sax, N. Irving, "Dangerous Properties of Industrial Materials", Van Nostrand Reinhold Co., 1975.

Fig. 1 View of a typical Fischer assay laboratory showing the following components: a) temperature controller; b) condensers; c) 2000-watt ovens; d) assembled glass adapters and 100 ml centrifuge tube; e) cooling bath; f) cast aluminum alloy retorts.

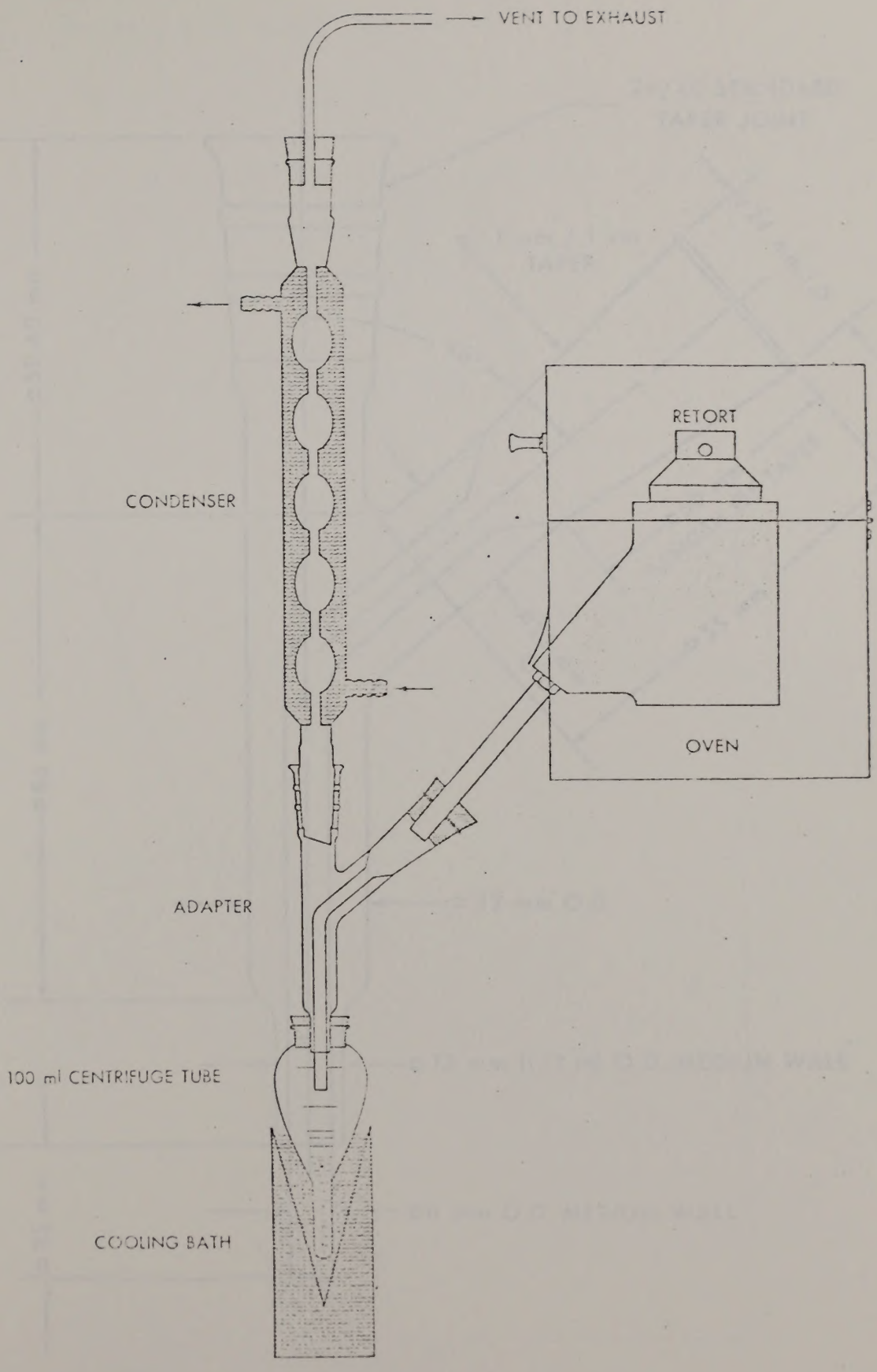


Fig. 2 Apparatus assembly

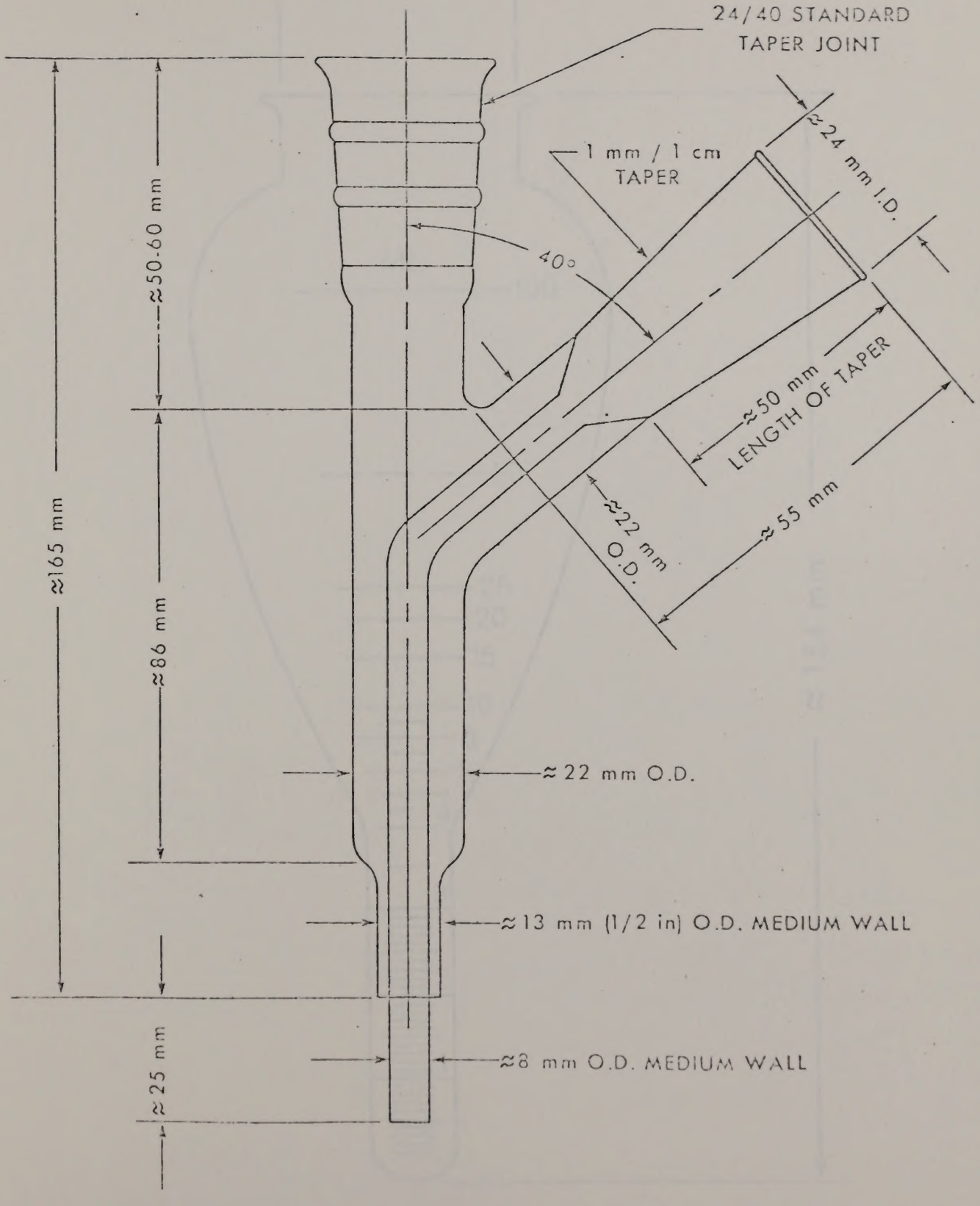


Fig. 3 Adapter

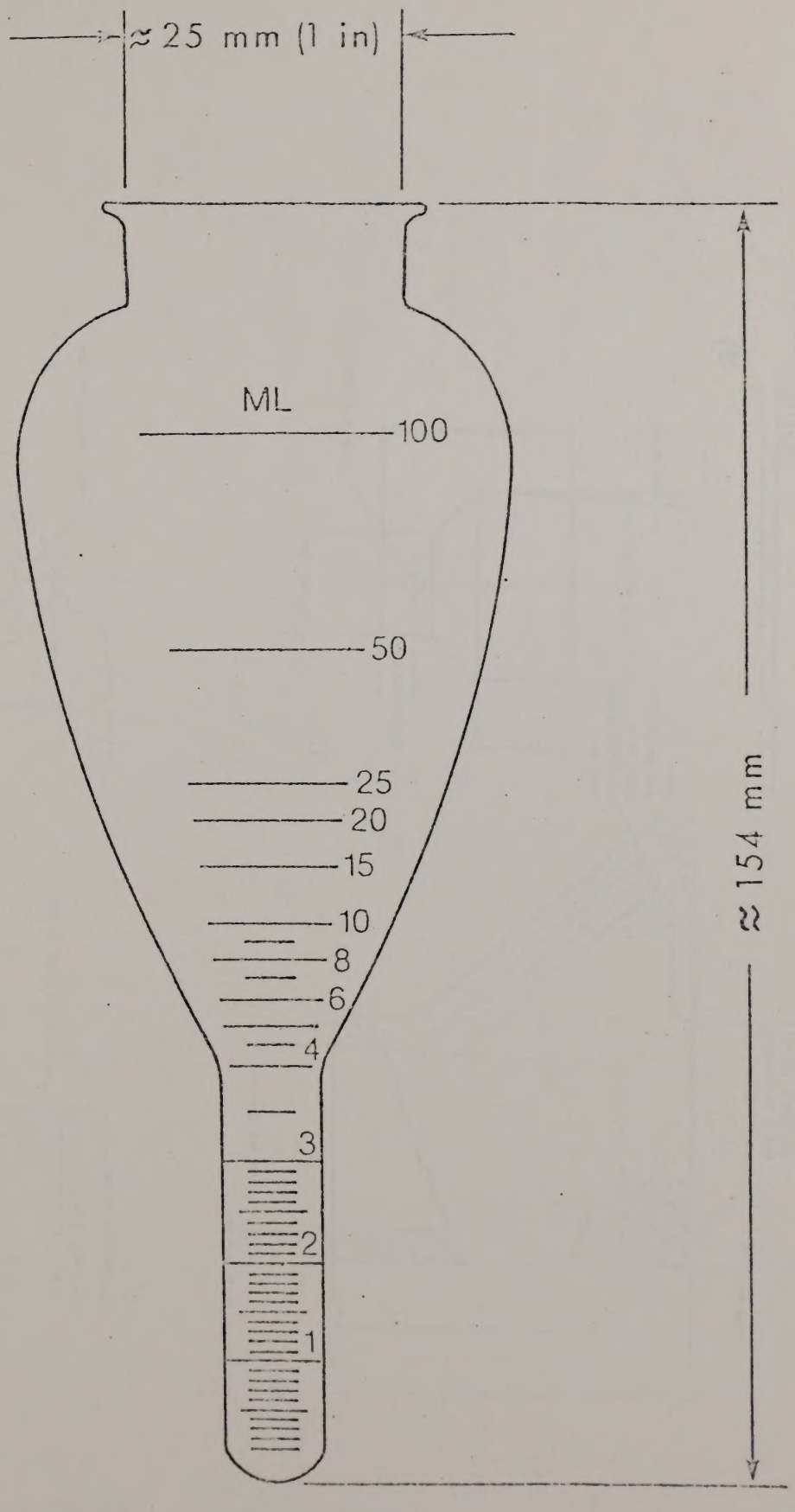
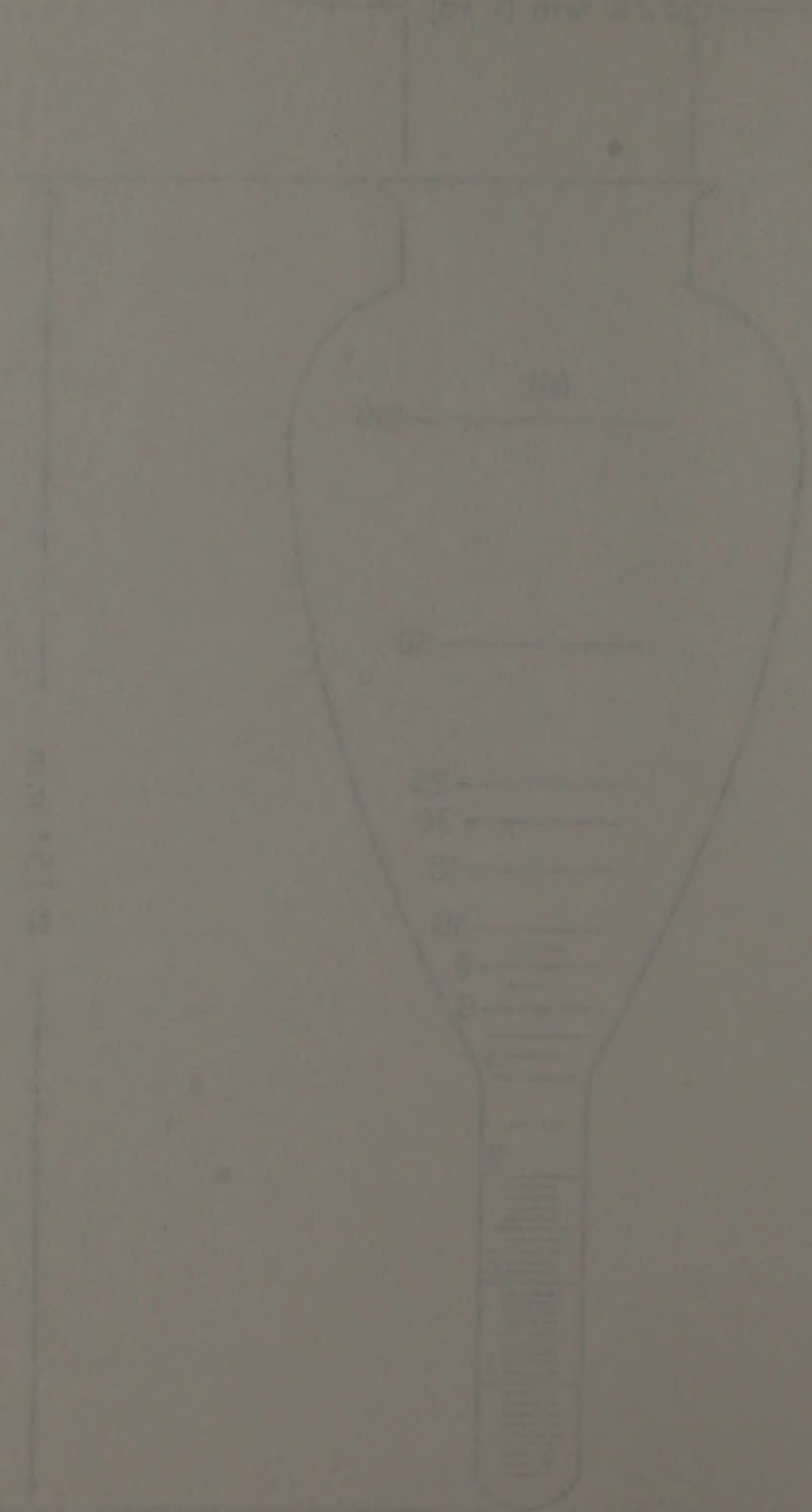


Fig. 4 100 ml centrifuge tube (receiver)



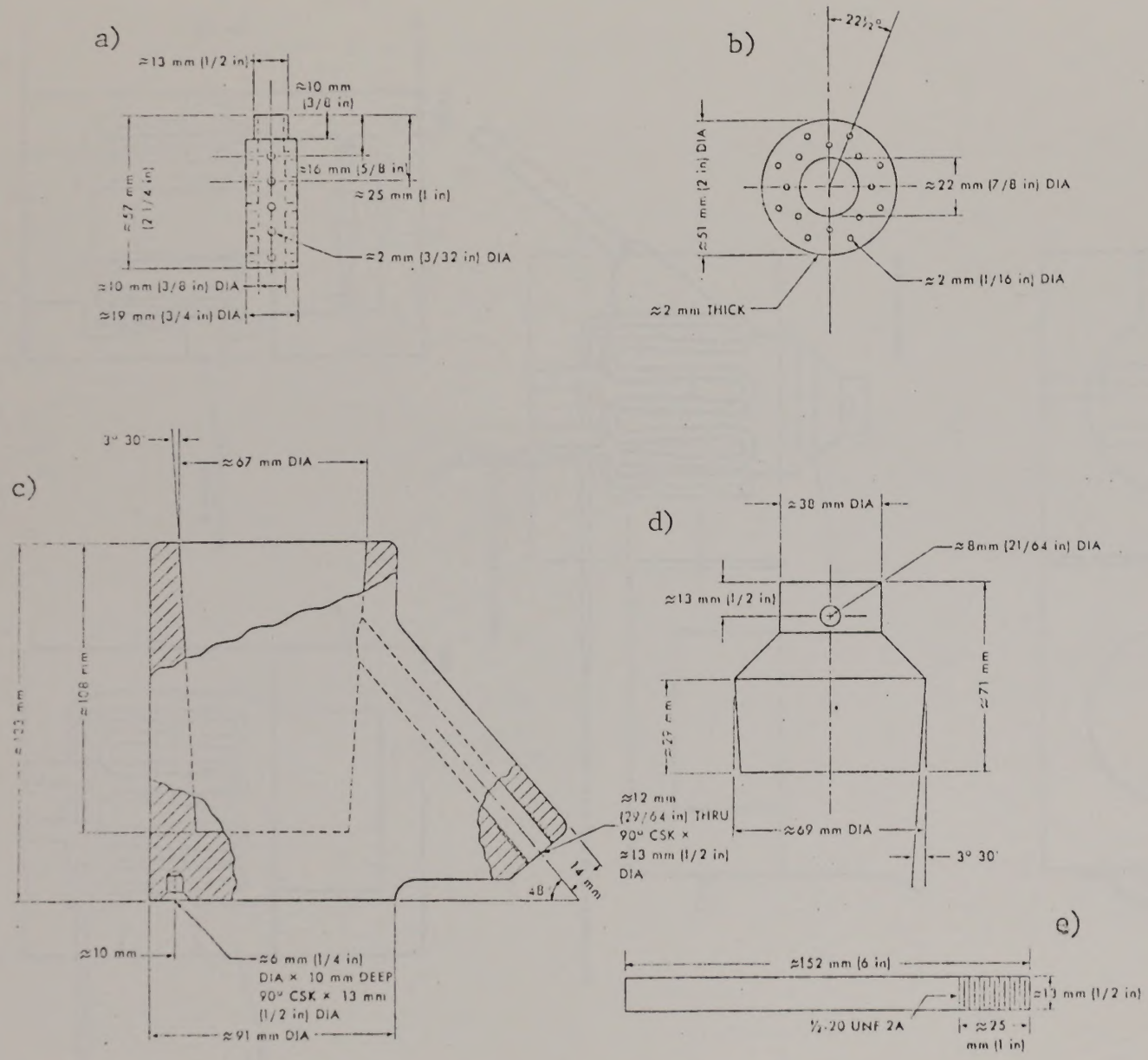


Fig. 5 Retort and components; a) aluminum chimney; b) aluminum disc; c) retort body; d) retort cap; and e) distillate outlet pipe.

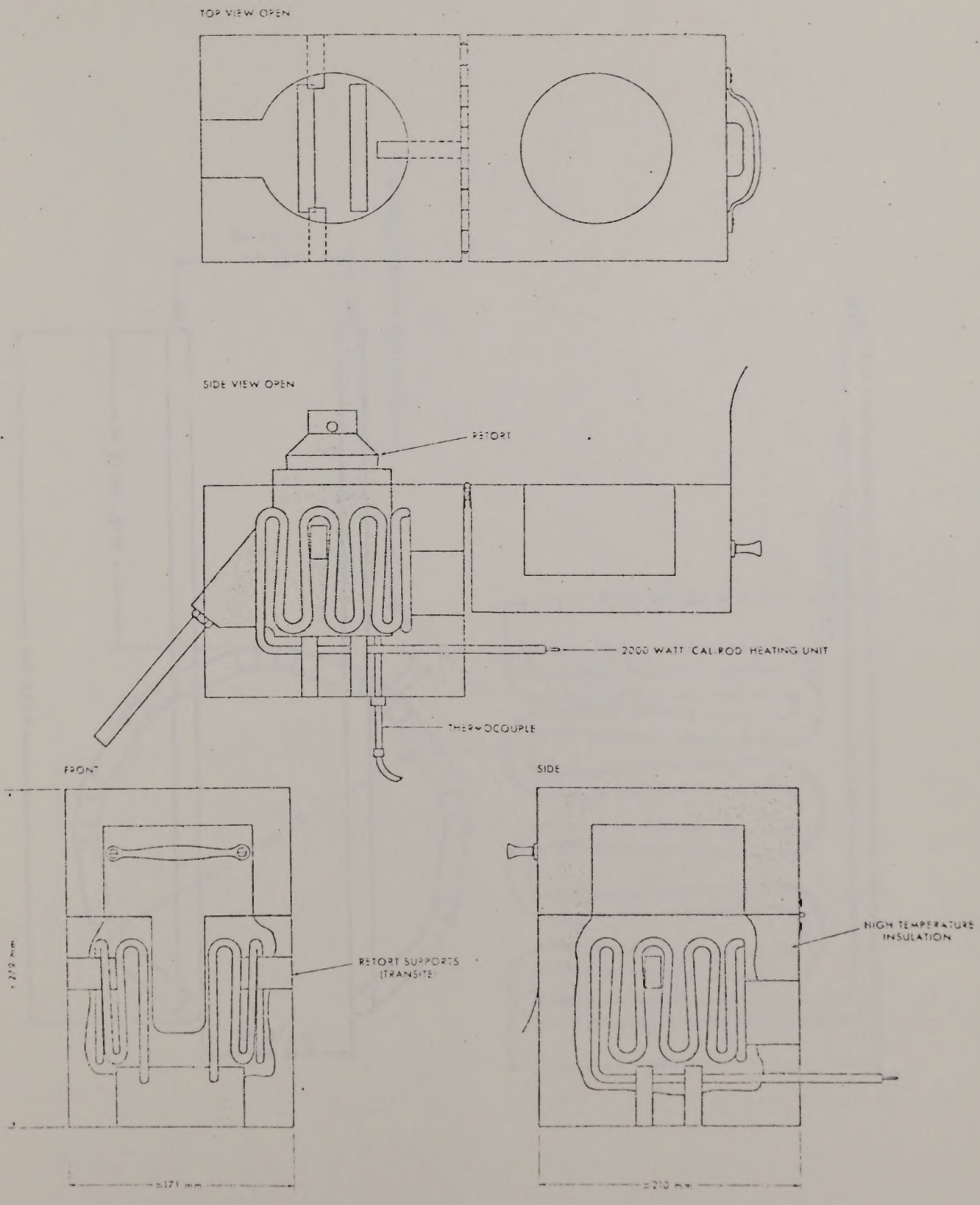
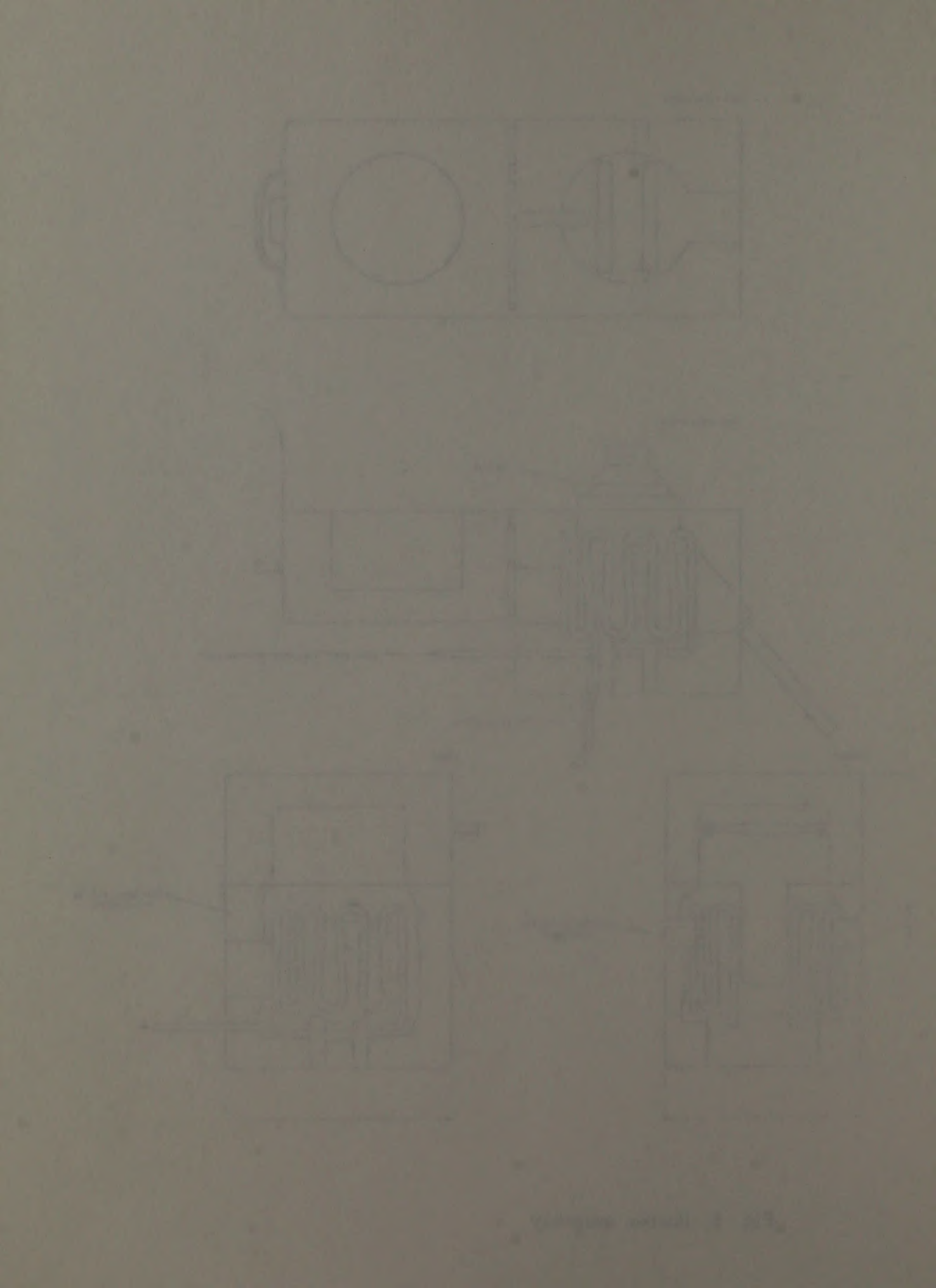


Fig. 6 Heater assembly



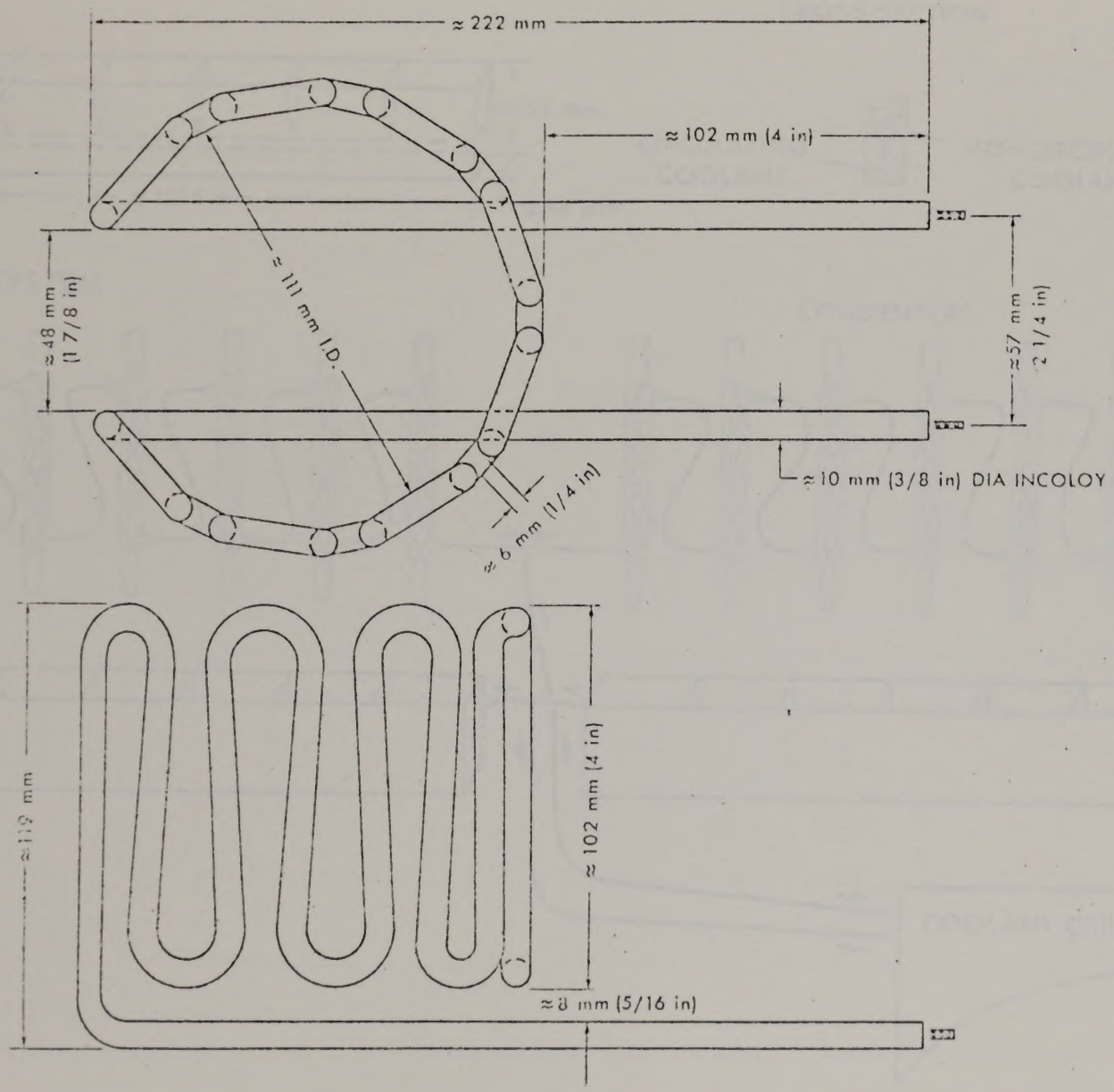


Fig. 7 2000-watt cal-rod heating element

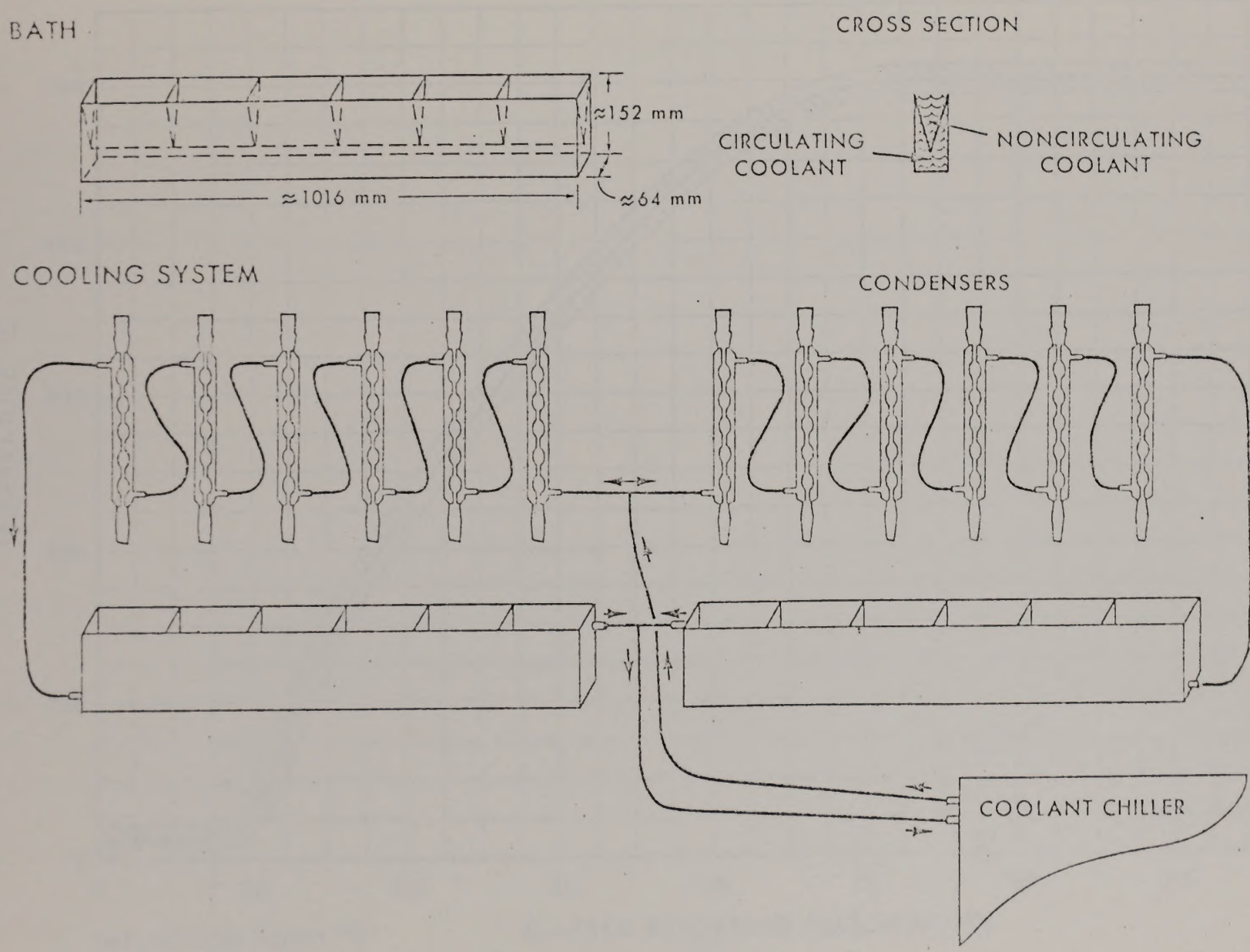
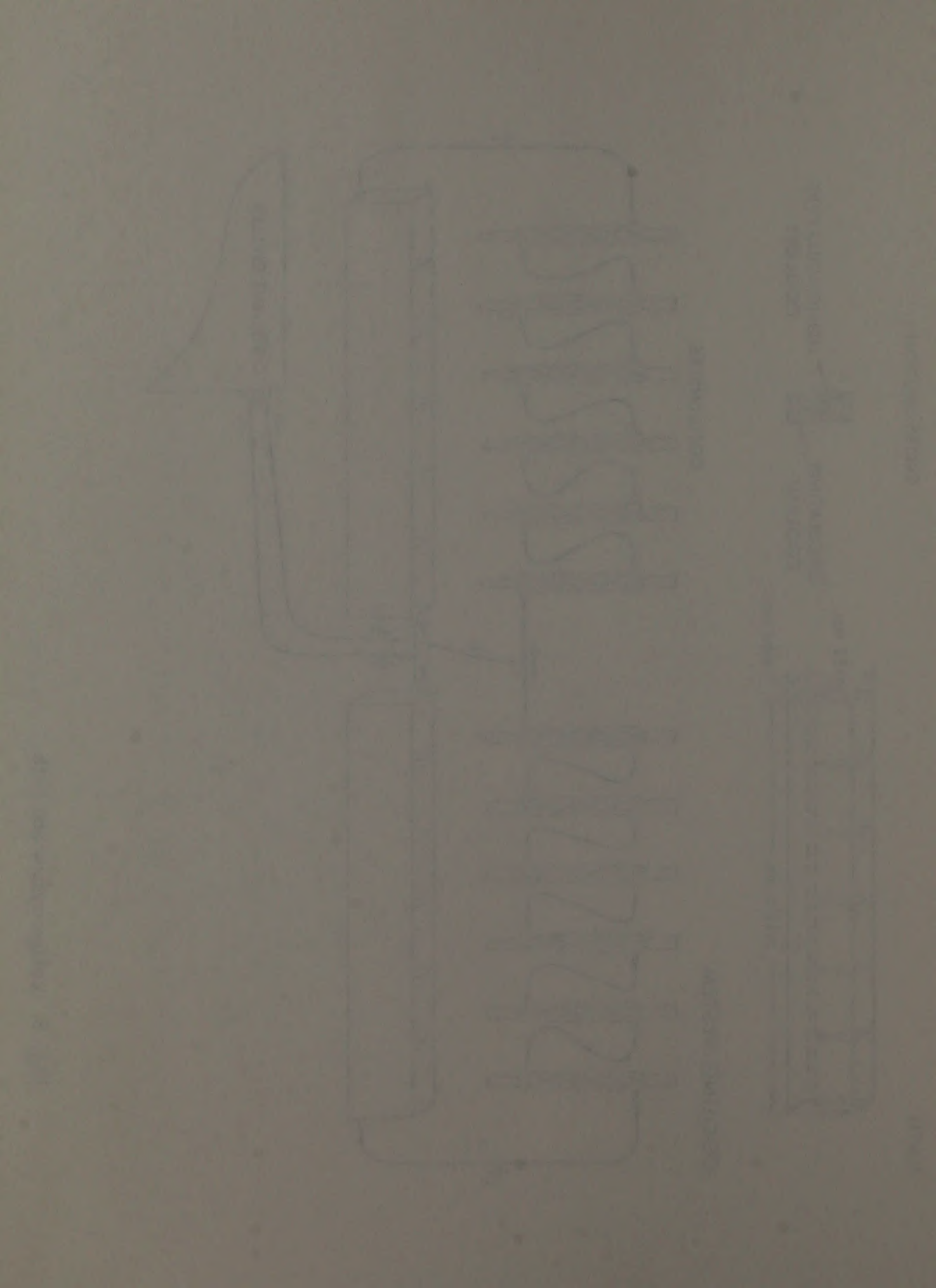


Fig. 8 Cooling system and bath



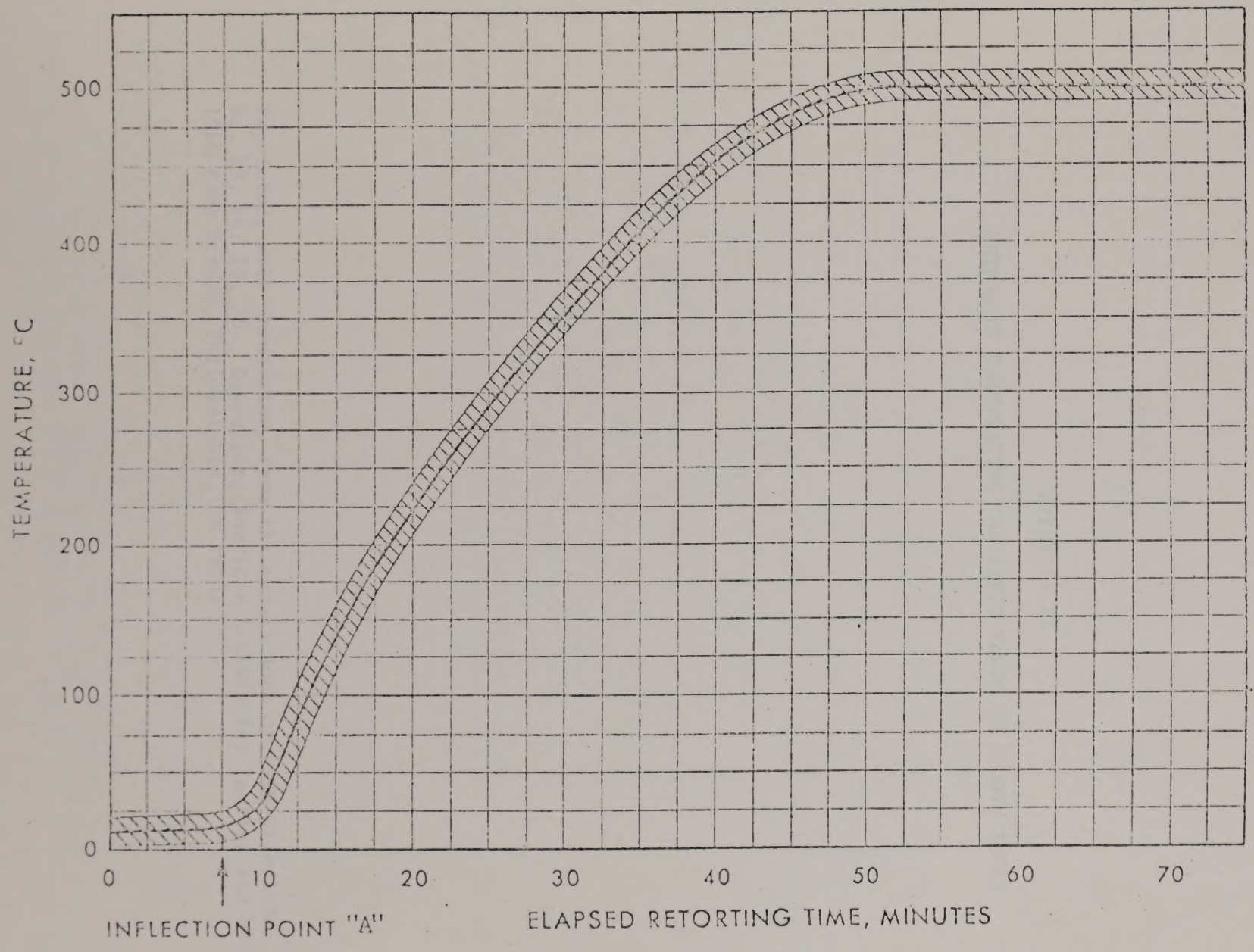


Fig. 9 Heating profile

APPENDIX II

METHOD OF CALCULATING CALORIFIC VALUE OF LIQUID FUELS

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Designation: D 240 – 64
(Reapproved 1973)

American National Standard Z11.14-1957 (R1974)
Reaffirmed March 18 1974
By American National Standards Institute
Method 2502—Federal Test
Method Standard No 791c

Standard Method of Test for HEAT OF COMBUSTION OF LIQUID HYDROCARBON FUELS BY BOMB CALORIMETER[1]

This Standard is issued under the fixed designation D 240; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval.

1. Scope

1.1 This method[2] covers the procedures for determining heat of combustion. It is applicable to a variety of substances but particularly to liquid hydrocarbon fuels of both low and high volatility

NOTE 1—The values stated in U.S. customary units are to be regarded as the standard

2. Summary of Method

2.1 Heat of combustion is determined in this method by burning a weighed sample in an oxygen bomb calorimeter under controlled conditions. The heat of combustion is computed from temperature observations before, during, and after combustion, with proper allowance for thermochemical and heat transfer corrections. Either isothermal or adiabatic calorimeter jackets may be used.

3. Definitions and Units

3.1 The energy units as used in this method are defined as follows:

3.1.1 *I cal* (International Table calorie) equals 4.1868 joules.

3.1.2 *I Btu* (British thermal unit) equals 251.996 cal equals 1055.06 joules.

3.2 *Gross Heat of Combustion*, expressed as calories per gram or British thermal units per pound—the heat released by the combustion of a unit mass of fuel in a constant volume bomb with substantially all of the water condensed to the liquid state.

3.3 *Net Heat of Combustion*, expressed as calories per gram or British thermal units per pound—the heat released by the combustion of a unit mass of fuel at a constant pressure of 1 atm with the water remaining in the vapor state (obtained by calculation from the determined gross heat of combustion).

3.4 *Energy Equivalent* (effective heat capacity or water equivalent) of the calorimeter is the energy required to raise the temperature 1 deg, expressed as calories per deg C or deg F.

3.5 *Temperatures* may be measured in either Fahrenheit or Celsius degrees.

NOTE 2—Temperatures may be recorded in ohms or other units when using electric thermometers. The same units must then be used in all calculations, including standardization.

3.6 *Time* is expressed in calculations in minutes and decimal fractions thereof. It may be measured in minutes and seconds.

3.7 *Weights* are measured in grams.

4. Apparatus

4.1 *Test Room*, *Bomb*, *Calorimeter*, *Jacket*, *Thermometers*, and *Accessories*, as described in Appendix A1.

5. Reagents

5.1 *Alkali, Standard Solution (0.0725 N)*—Dissolve 3.84 g of Na_2CO_3 in water and

[1] This method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants.

Current edition effective Aug. 31, 1964. Originally issued 1926. Replaces D 240 – 57 T.

[2] A more precise method designed specifically for use with aviation turbine fuels, although it can be used for a wide range of volatile and nonvolatile fuels, is described in ASTM Method D 2382, Test for Heat of Combustion of Hydrocarbon Fuels by Bomb Calorimeter (High-Precision Method), *Annual Book of ASTM Standards*, Part 24

... to 1 liter; alterna... ...de (NaOH) or pot... ...(II) solutions of the p... ...cceptable.

... *Benzoic Acid, Stand...* ...der must be compresse... ...t before weighing. Be... ...which the heat of cor... ...termined by comparison ...reau of Standards sam... ...mmercially for those ...upped to pellet benzoic a...

... *Methyl Orange or ...ator.*

... *Oxygen*—Commerica... ...from liquid air can general... ...purification. If purificatior... ...Appendix A1, A1.11.

... *2,2,4-Trimethylpent... Standard.*[4]

6. Standardization

6.1 Determine the energy ...alorimeter as the average ... tests using standard benzoi... should be spaced over a ... than three days. Use not l... more than 1.1 g of stan... (C_6H_5COOH). Make ea... according to the procedure ...tion 7 and compute the cor... rise, *t*, as described in 8.1 the corrections for nitric ... firing wire as described in ... in the following equation:

$$W = (Hg + e_1 -$$

where:

- W = energy equivalent ... cal/deg F or C (J/K)
- H = heat of combustion o... acid, 6318 cal/g (26.4...
- g = weight of standard ... ple, g,
- t = corrected temperatu... lated in 8.1 or 8.2,
- e_1 = correction for heat o... tric acid, cal (J) and
- e_2 = correction for heat ... firing wire, cal (J).

6.1.1 Standardization te... ...ted after changing any p... ...r and occasionally as a c...

dilute to 1 liter; alternatively, sodium hydroxide (NaOH) or potassium hydroxide (KOH) solutions of the prescribed normality are acceptable.

5.2 *Benzoic Acid, Standard*[3]—Benzoic acid powder must be compressed into a tablet or pellet before weighing. Benzoic acid pellets for which the heat of combustion has been determined by comparison with the National Bureau of Standards sample are obtainable commercially for those laboratories not equipped to pellet benzoic acid.

5.3 *Methyl Orange or Methyl Red Indicator.*

5.4 *Oxygen*—Commerical oxygen produced from liquid air can generally be used without purification. If purification is necessary see Appendix A1, A1.11.

5.5 *2,2,4-Trimethylpentane* (*iso*octane), *Standard.*[4]

6. Standardization

6.1 Determine the energy equivalent of the calorimeter as the average of not less than six tests using standard benzoic acid. These tests should be spaced over a period of not less than three days. Use not less than 0.9 g nor more than 1.1 g of standard benzoic acid (C_6H_5COOH). Make each determination according to the procedure described in Section 7 and compute the corrected temperature rise, t, as described in 8.1 or 8.2. Determine the corrections for nitric acid (HNO_3) and firing wire as described in 8.3 and substitute in the following equation:

$$W = (Hg + e_1 + e_3)/t$$

where:

W = energy equivalent of calorimeter, cal/deg F or C (J/K)
H = heat of combustion of standard benzoic acid, 6318 cal/g (26.454 J/g)
g = weight of standard benzoic acid sample, g,
t = corrected temperature rise, as calculated in 8.1 or 8.2,
e_1 = correction for heat of formation of nitric acid, cal (J) and
e_3 = correction for heat of combustion of firing wire, cal (J).

6.1.1 Standardization tests should be repeated after changing any part of the calorimeter and occasionally as a check on both calorimeter and operating technique.

6.2 *Checking the Calorimeter for Use with Volatile Fuels*—Use National Bureau of Standards standard sample No. 217b (5.5) to determine whether the results obtained agree with the certified value (20,545 Btu/lb (47.788 MJ/kg), weight in air) within the repeatability of the method. If results do not come within this range, the method of handling the sample may have to be changed (Appendix A1, A1.8). If this is not possible or does not correct the error, run a series of tests using standard sample No. 217b to establish the energy equivalent for use with volatile fuels.

7. Procedure

7.1 *Weight of Sample*—Control the weight of sample (including any auxiliary fuel) so that the temperature rise produced by its combustion will be equal to that of 0.9 to 1.1 g of benzoic acid (Note 3). Weigh the sample to the nearest 0.1 mg.

NOTE 3—If the approximate heat of combustion of the sample is known, the required weight can be estimated as follows:

$$g = 11{,}373/h_1$$

where:
g = weight of sample, g, and
h_1 = approximate heat of combustion of sample, Btu/lb.

or

$$g = 26.454/h_1$$

where h_1 is in MJ/kg

7.2 *Water in Bomb*—Add 1.0 ml of water to the bomb from a pipet.

7.3 *Oxygen*—With the test sample and fuse in place, charge the bomb with oxygen to 30 atm (3.0 MN/m²) gage pressure at room temperature (Note 4). Do *not* purge the bomb to remove entrapped air. **Caution**—Be careful not to overcharge the bomb. If, by accident, the oxygen introduced into the bomb should exceed 40 atm (4.0 MN/m²), *do not* proceed with the combustion. An explosion might occur with possible violent rupture of the bomb. Detach the filling connection and exhaust the bomb in the usual manner. Discard the sample, unless it has lost no weight,

[3] Obtainable from the Nat. Bureau Standards, Washington, D. C. 20234, as standard sample No. 39i.

[4] Obtainable from the Nat. Bureau Standards, Washington D. C. 20234, as standard sample No. 217b.

as shown by reweighing.

NOTE 4—Lower or higher initial oxygen pressures may be used within the range from 25 to 35 atm (2.5 to 3.5 MN/m²), provided the same pressure is used for all tests, including standardization.

7.4 *Calorimeter Water*—Adjust the calorimeter water temperature before weighing as follows:

Isothermal jacket method	3.0 to 3.5 F (1.6 to 2.0 C) below jacket temperature (Note 5).
Adiabatic jacket method (7.6)	2.0 to 2.5 F (1.0 to 1.4 C) below room temperature.

NOTE 5—This initial adjustment will ensure a final temperature slightly above that of the jacket for calorimeters having an energy equivalent of approximately 2450 cal/deg C (10,200 J/K). Some operators prefer a lower initial temperature so that the final temperature is slightly below that of the jacket. This procedure is acceptable, provided it is used in all tests, including standardization.

7.4.1 Use the same amount (±0.5 g) of distilled or deionized water in the calorimeter vessel for each test. The amount of water (2000 g is usual) can be most satisfactorily determined by weighing the calorimeter vessel and water together on a balance. The water may be measured volumetrically if it is measured always at the same temperature.

7.5 *Observations, Isothermal Jacket Method*—Assemble the calorimeter in the jacket and start the stirrer. Allow 5 min for attainment of equilibrium; then record the calorimeter temperatures (Note 6) at 1-min intervals for 5 min. Fire the charge at the start of the sixth minute and record the time and temperature, t_a. Add to this temperature 60 percent of the expected temperature rise, and record the time at which the 60 percent point is reached (Note 7). After the rapid rise period (about 4 to 5 min), record temperatures at 1-min intervals on the minute until the *difference* between successive readings has been constant for 5 min.

NOTE 6—Use a magnifier and estimate all readings (except those during the rapid rise period) to the nearest 0.005 F or 0.002 C when using ASTM Bomb Calorimeter Thermometers 56F or 56C. Estimate Beckmann thermometer readings to the nearest 0.001 C and 25-Ω resistance thermometer readings to the nearest 0.0001 Ω. Tap mercurial thermometers with a pencil just before reading to avoid errors caused by mercury sticking to the walls of the capillary.

NOTE 7—When the approximate expected rise is unknown, the time at which the temperature reaches 60 percent of the total can be determined by recording temperatures at 45, 60, 75, 90, and 105 s after firing and interpolating.

7.6 *Observations, Adiabatic Jacket Method* (*Note 8*)—Assemble the calorimeter in the jacket and start the stirrers. Adjust the jacket temperature to be equal to or slightly lower than the calorimeter, and run for 5 min to obtain equilibrium. Adjust the jacket temperature to match the calorimeter within ±0.02 F (0.01 C) and hold for 3 min. Record the initial temperature (Note 6) and fire the charge. Adjust the jacket temperature to match that of the calorimeter during the period of rise, keeping the two temperatures as nearly equal as possible during the rapid rise, and adjusting to within ±0.02 F (0.01 C) when approaching the final equilibrium temperature. Take calorimeter readings at 1-min intervals until the *same* temperature is observed in three successive readings. Record this as the final temperature. Time intervals are not recorded as they are not critical in the adiabatic method.

NOTE 8—These instructions supersede the instructions given in 7.5 when using jackets equipped for adiabatic temperature control.

7.7 *Analysis of Bomb Contents*—Remove the bomb and release the pressure at a uniform rate such that the operation will require not less than 1 min. Examine the bomb interior for evidence of incomplete combustion. Discard the test if unburned sample or sooty deposits are found.

7.7.1 Wash the interior of the bomb, including the electrodes and sample holder, with a fine jet of water and quantatively collect the washings in a beaker. Use a minimum of wash water, preferably less than 350 ml. Titrate the washings with standard alkali solution, using methyl orange or methyl red indicator.

7.7.2 Remove and measure the combined pieces of unburned firing wire, and subtract from the original length. Record the difference as "wire consumed."

7.7.3 Determine the sulfur content of the sample if it exceeds 0.1 percent. Determine sulfur by analyzing the bomb washings remaining after the acid titration, using the procedure described in ASTM Method D 129, Test for Sulfur in Petroleum Products by the Bomb Method.[5]

[5] *Annual Book of ASTM Standards*, Part 23.

8. Calculations

8.1 *Temperature Rise in I Calorimeter*—Using data scribed in 7.5, compute the te in an isothermal jacket calori

$$t = t_c - t_a - r_1(b - a)$$

where:

- t = corrected temperature r
- a = time of firing,
- b = time (to nearest 0.1 temperature rise reache total,
- c = time at beginning of per rate of temperature ch has become constant (aft
- t_a = temperature at time of for thermometer error (
- t_c = temperature at time, thermometer error (Not
- r_1 = rate (temperature units which temperature was min period before firing.
- r_2' = rate (temperature units which temperature was 5-min period after time ature is falling, r_2 is r quantity $-r_2(c - b)$ is p

NOTE 9—All mercury-in-gl must be corrected for scale erro the thermometer certificate presc A1, A1.5.1 or A1.5.2. Beckmann require a setting correction and correction (Appendix A2, A2 ASTM Thermometers 56F and 5 emergent stem corrections if a standardization, are performed w F (5.5 C) interval. If operating te this limit, a differential emerger (Appendix A2, A2.1.1) must be rected temperature rise, t, in a standardization.

8.2 *Temperature Rise in Calorimeter*—Using data o scribed in 7.6, compute the t t, in an adiabatic jacket cal lows:

$$t = t_f - t_a$$

where:

- t = corrected temperature r
- t_a = temperature when charg rected for thermometer and
- t_f = final equilibrium tempe for thermometer error

8. Calculations

8.1 *Temperature Rise in Isothermal Jacket Calorimeter*—Using data obtained as prescribed in 7.5, compute the temperature rise, t, in an isothermal jacket calorimeter as follows:

$$t = t_c - t_a - r_1(b - a) - r_2(c - b) \quad (1)$$

where:

t = corrected temperature rise,
a = time of firing,
b = time (to nearest 0.1 min) when the temperature rise reaches 60 percent of total,
c = time at beginning of period in which the rate of temperature change with time has beeome constant (after combustion),
t_a = temperature at time of firing, corrected for thermometer error (Note 9),
t_c = temperature at time, c, corrected for thermometer error (Note 9),
r_1 = rate (temperature units per minute) at which temperature was rising during 5-min period before firing, and
r_2 = rate (temperature units per minute) at which temperature was rising during the 5-min period after time c. If the temperature is falling, r_2 is negative and the quantity $-r_2(c - b)$ is positive.

NOTE 9—All mercury-in-glass thermometers must be corrected for scale error, using data from the thermometer certificate prescribed in Appendix A1, A1.5.1 or A1.5.2. Beckmann thermometers also require a setting correction and an emergent stem correction (Appendix A2, A2.1.2). Solid-stem ASTM Thermometers 56F and 56C do not require emergent stem corrections if all tests, including standardization, are performed within the same 10 F (5.5 C) interval. If operating temperatures exceed this limit, a differential emergent stem correction (Appendix A2, A2.1.1) must be applied to the corrected temperature rise, t, in all tests, including standardization.

8.2 *Temperature Rise in Adiabatic Jacket Calorimeter*—Using data obtained as prescribed in 7.6, compute the temperature rise, t, in an adiabatic jacket calorimeter as follows:

$$t = t_f - t_a \quad (2)$$

where:

t = corrected temperature rise,
t_a = temperature when charge was fired, corrected for thermometer error (Note 9), and
t_f = final equilibrium temperature, corrected for thermometer error (Note 9).

8.3 *Thermochemical Corrections (Appendix)*—Compute the following for each test:

e_1 = correction for heat of formation of nitric acid (HNO_3), cal (1 cal = 4.1868 J),
= milliliters standard alkali solution used in acid titration,
e_2 = correction for heat of formation of sulfuric acid (H_2SO_4), cal (1 cal = 4.1868 J),
= 14 × percentage of sulfur in sample × weight of sample, g,
e_3 = correction for heat of combustion of firing wire, cal (1 cal = 4.1868 J),
= 0.27 × millimeters of iron wire consumed,
= 0.23 × millimeters of Chromel C wire consumed.

8.4 *Gross Heat of Combustion*—Compute the gross heat of combustion by substituting in the following equation:

$$H_g = (tW - e_1 - e_2 - e_3)/g \quad (3)$$

where:

H_g = gross heat of combustion, cal/g (1 cal/g = 4.1868 J/g),
t = corrected temperature rise as calculated in 8.1 or 8.2,
W = energy equivalent of calorimeter, cal/deg F or C (1 cal/deg F = 2.326 J/deg C, 1 cal/deg C = 4.1868 J/deg C) (Section 6),
e_1, e_2, e_3 = corrections as prescribed in 8.3, and
g = weight of sample, g.

9. Reporting Results

9.1 Usually the gross heat of combustion, H_g, in Btu per pound (obtained by multiplying H_g by 1.8) should be reported for fuel oils in preference to net heat of combustion, because of the difficulty in accurately determining the hydrogen content of the samples.

9.2 If the percentage of hydrogen, H, in the sample is known, the net heat of combustion may be calculated as follows:

$$H_n = 1.8\,H_g - 91.23 \times H \quad (4)$$

where:

H_n = net heat of combustion, Btu/lb (1 Btu/lb 2.326 kJ/kg),
H_g = gross heat of combustion, cal/g (1 cal/g = 4.1868 kJ/kg), and
H = hydrogen in the sample, percent.

9.3 If the percentage of hydrogen in avia-

tion gasoline and turbine fuel samples is not known, the net heat of combustion may be calculated as follows:[6]

$$H_n = 4310 + (0.7195)(1.8)(H_g) \quad (5)$$

where:

H_n = net heat of combustion, Btu/lb (1 Btu/lb = 2.326 kJ/kg), and

H_g = gross heat of combustion, cal/g (1 cal/g = 4.1868 kJ/kg).

10. Precision[7]

10.1 The following criteria should be used for judging the acceptability of results (95 percent confidence):

10.1.1 *Repeatability*—Duplicate results by the same operator should be considered suspect if they differ by more than the following amount:

Repeatability	55 Btu/lb (130 kJ/kg)

10.1.2 *Reproducibility*—Results submitted by two or more laboratories should be considered suspect if they differ by more than the following amount:

Reproducibility	175 Btu/lb (400 kJ/kg)

[6] Equation 5 is recommended only if the percentage of hydrogen is not known. It is based on Eq 4 and an empirical relation between H and the percentage of hydrogen in aviation gasolines and turbine fuels, developed from data by R. S. Jessup and C. S. Cragoe, "Net Heat of Combustion of AN-F-28 Aviation Gasolines," Nat. Advisory Committee for Aeronautics, *Technical Note No. 996*, June, 1945, and Joseph A. Cogliano and Ralph S. Jessup, "Relation Between Net Heat of Combustion and Aniline-Gravity Product of Aircraft Fuels," Nat. Bureau of Standards *Report 2348*, March, 1953.

[7] The summary of cooperative test data from which these repeatability and reproducibility values were calculated was published for information as Appendix XII to the 1957 Report of Committee D-2 on Petroleum Products and Lubricants. The summary of test data was also published from 1958 to 1966, inclusive, as Appendix III to ASTM Method D 240. The data are now filed at ASTM Headquarters as Research Report No. RR 38: D-2.

APPENDIXES

A1. APPARATUS

A1.1 *Test Room*—The room in which the calorimeter is operated must be free from drafts and not subject to sudden temperature changes. The direct rays of the sun shall not strike the jacket or thermometers. Adequate facilities for lighting, heating, and ventilating shall be provided. Thermostatic control of room temperature, and controlled relative humidity are desirable.

A1.2 *Oxygen Bomb*—The oxygen bomb shall have an internal volume of 350 ± 50 ml. All parts shall be constructed of materials which are not affected by the combustion process or products sufficiently to introduce measurable heat input or alteration of end products. If the bomb is lined with platinum or gold, all openings shall be sealed to prevent combustion products from reaching the base metal. The bomb must be designed so that all liquid combustion products can be completely recovered by washing the inner surfaces. There must be no gas leakage during a test. The bomb must be capable of withstanding a hydrostatic pressure test to 3000 psig (20 MN/m^2) at room temperature without stressing any part beyond its elastic limit.

A1.3 *Calorimeter*—The calorimeter (Note A1) vessel shall be made of metal (preferably copper or brass) with a tarnish-resistant coating, and with all outer surfaces highly polished. Its size shall be such that the bomb will be completely immersed in water when the calorimeter is assembled. It shall have a device for stirring the water thoroughly and at a uniform rate, but with minimum heat input. Continuous stirring for 10 min shall not raise the calorimeter temperature more than 0.01 C starting with identical temperatures in the calorimeter, room, and jacket. The immersed portion of the stirrer shall be coupled to the outside through a material of low heat conductivity.

NOTE A1—As used in this method, the term "calorimeter" designates the bomb, the vessel with stirrer, and the water in which the bomb is immersed.

A1.4 *Jacket*—The calorimeter shall be completely enclosed within a stirred water jacket and supported so that its sides, top, and bottom are approximately 10 mm from the jacket walls. The jacket may be arranged so as to remain at substantially constant temperature, or with provision for rapidly adjusting the jacket temperature to equal that of the calorimeter for adiabatic operation. It must be constructed so that any water evaporating from the jacket will not condense on the calorimeter.

A1.4.1 A double-walled jacket with a dead-air insulation space may be substituted for the constant-temperature water jacket if the calorimeter is operated in a constant-temperature (±2 F) (±1 C) room. The same ambient conditions must be maintained for all experiments, including standardization.

A1.5 *Thermometers*—Temperatures in the calorimeter and jacket shall be measured with the following thermometers or combinations thereof:

A1.5.1 *Etched Stem, Mercury-in-Glass, ASTM Bomb Calorimeter Thermometer* having a range from 66 to 95 F or 19 to 35 C, 18.9 to 25.1 C, or 23.9 to 30.1 C, as specified, and conforming to the requirements for Thermometer 56F, 56C, 116C, or 117C, respectively, as prescribed in ASTM Specification E 1 for Thermometers.[8] Each of these thermometers shall have been test
intervals no larger than 2.5 F
tire graduated scale. Correctio
to 0.005 F or 0.002 C, respec
point.

A1.5.2 *Beckmann Differen*
range 6 C reading upward as s
ing to the requirements for T
prescribed in Specification E
mometers shall be tested for
no larger than 1 C over the
and corrections reported to
point.

A1.5.3 *Calorimetric Type Thermometer, 25-Ω.*

A1.6 *Thermometer Access*
required for reading mercury-
to one tenth of the smallest sca
have a lens and holder designe
duce significant errors due to

A1.6.1 A Wheatstone brid
capable of measuring resistan
necessary for use with resistanc

A1.7 *Timing Device*—A w
device capable of measuring t
for use with the isothermal jac

A1.8 *Sample Holder*—Non
be burned in an open crucible
red), quartz or acceptable ba
metal alloy crucibles are acce
preliminary firings the weight
nificantly between tests.

A1.8.1 Volatile samples sh

A2.1 Thermometer Correctio

A2.1.1 The differential em
for solid stem calorimetric th
56C) may be computed from

Differential stem correction
= $K(t_c$ –

where:

K = differential expansion
in glass = 0.00016 for
or 0.00009 for Fahrenh
L = scale reading to which
immersed,
T = mean temperature of e
t_o = initial temperature rea
t_c = final temperature readi

A2.1.2 Differential emerg
a Beckmann thermometer i
the scale may be computed as

Differential stem correction
= $K(t$

where:

S = the "setting" (temperat
the thermometer,
K, T, t_c, and t_o as defined in A

A2.1.3 "Setting" correct
thermometer may be comput

"Setting" correction =

[8] *Annual Book of ASTM Standards*, Parts 25 and 44.

Designation: D 2382 – 65 (Reapproved 1975)

American National Standard Z11.192-1966
American National Standards Institute
Federal Test Method Standard No. 791b

Standard Method of Test for HEAT OF COMBUSTION OF HYDROCARBON FUELS BY BOMB CALORIMETER (HIGH-PRECISION METHOD)[1]

This Standard is issued under the fixed designation D 2382; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval.

...t rights in connection there-
...yone utilizing the standard

1. Scope

1.1 This method covers the determination of the heat of combustion of hydrocarbon fuels. It is designed specifically for use with aviation turbine fuels when the permissible difference between duplicate determinations is of the order of 0.1 percent (Note 1). It can be used for a wide range of volatile and nonvolatile materials where slightly greater differences in precision can be tolerated.

NOTE 1—In order to attain this accuracy, strict adherence to all details of the procedure is essential since the error contributed by each individual measurement that affects the accuracy must be kept below 0.02 percent, insofar as possible.

2. Summary of Method

2.1 The heat of combustion is determined by burning a weighed sample in an oxygen-bomb calorimeter under controlled conditions. The temperature is measured by means of a platinum resistance thermometer. The heat of combustion is calculated from temperature observations before, during, and after combustion, with proper allowance for thermochemical and heat-transfer corrections. Either isothermal or adiabatic calorimeters may be used.

3. Units and Definitions

3.1 The energy units used in this method are defined as follows:

1 cal (International Table calorie) = 4.1868 absolute joules.

1 Btu (British thermal unit) = 251.996 cal = 1055.06 absolute joules.

1 cal/g = 1.8 Btu/lb.

3.2 *Gross Heat of Combustion*, expressed as calories per gram or British thermal units per pound. The gross heat of combustion at constant volume of a liquid or solid fuel containing only the elements carbon, hydrogen, oxygen, nitrogen, and sulfur is the quantity of heat liberated when a unit weight of the fuel is burned in oxygen in an enclosure of constant volume, the products of combustion being gaseous carbon dioxide, nitrogen, sulfur dioxide, and liquid water, with the initial temperature of the fuel and the oxygen and the final temperature of the products at 25 C. Gross heat of combustion[2] is represented by the symbol Q_g.

3.3 *Net Heat of Combustion*, expressed as calories per gram or British thermal units per

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[1] This method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants.

Effective Aug. 31, 1965.

[2] Users of this method desiring to calculate $\Delta H°_{c_{298}}$ for a pure compound should note that corrections must be applied to the value of Q_g for buoyancy of air, heat capacities of reaction components, reduction to a constant-pressure process, and deviations of the reaction from the thermodynamic standard state. See, for example Prosen, E. J., "Experimental Thermochemistry," F. D. Rossini, editor, Interscience Publishers, 1956, pp. 129-148. Reliable values for heats of combustion of pure compounds are given in National Bureau of Standards *Circular C-461*, "Selected Values of Properties of Hydrocarbons" (U. S. Government Printing Office, Washington, D. C., 1947) and in F. D. Rossini, et al, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953. These compilations were prepared by F. D. Rossini, et al as part of American Petroleum Institute Research Project 44. In any comparison of measurements on pure compounds with those cited in these compilations, the user of this method should realize that impurities of various kinds, including water and foreign hydrocarbons may cause significant effects on the values obtained for particular samples of material.

pound. The net heat of combustion at constant pressure of a liquid or a solid fuel containing only the elements carbon, hydrogen, oxygen, nitrogen, and sulfur is the quantity of heat liberated when a unit weight of the fuel is burned in oxygen at a constant pressure of 1 atm, the products of combustion being carbon dioxide, nitrogen, sulfur dioxide, and water, all in the gaseous state, with the initial temperature of the fuel and the oxygen and the final temperature of the products of combustion at 25 C. The net heat of combustion[3] is represented by the symbol Q_n and is related to the gross heat of combustion by the following equation:

$$Q_n \text{ (net, 25 C)} = Q_g \text{ (gross, 25 C)} - 91.23 \times H$$

where:

Q_n (net, 25 C) = net heat of combustion at constant pressure, Btu/lb.

Q_g (gross, 25 C) = gross heat of combustion at constant volume, Btu/lb.

H = weight percent by hydrogen in the sample.

3.4 *Energy Equivalent (Effective Heat Capacity or Water Equivalent)*—The energy equivalent of the calorimeter expressed as calories per ohm is the energy required to raise the temperature of the calorimeter 1 Ω.

NOTE 2—The conversion of resistance in ohms to temperature in degrees Celsius is not strictly a straight line function, but if the mean temperature of the experiment is kept within reasonable limits (the mean value of the initial and final resistance within 0.1 Ω of a previously established value), no significant error is introduced.[3]

3.5 *Temperatures* are measured in ohms (see Note 2).

3.6 *Time* is expressed in minutes and decimal fractions thereof. It may be measured in minutes or seconds, or both.

3.7 *Weights* are measured in grams.

4. Apparatus

4.1 *Test Room, Bomb, Calorimeter, Jacket, Thermometers, and Accessories*, as described in Appendix A1.

4.2 *Semimicro Analytical Balance*, having a sensitivity of 0.01 mg as specified in 9.5.1.

4.3 *Heavy-Duty Analytical Balance*, having a sensitivity of 0.05 g as specified in 9.7.2.

NOTE 3—The resistance thermometer used in this method is of the four-terminal type having both current and potential leads and is made for use with a commutator. In bomb calorimetric measurements where only a small temperature range is to be measured, it is permissible to omit the commutator.

5. Reagents and Materials

5.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[4] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to ASTM Specification D 1193, for Reagent Water.[5]

5.3 *Benzoic Acid*[6]—The acid must be pelleted before use.

5.4 *Firing Wire*—No. 36 gage (0.127-mm) platinum wire, cut in 100-mm lengths.

5.5 *Methyl Red Indicator.*

5.6 *Oxygen*—Commercial oxygen produced from liquid air can be used without purification. Oxygen prepared by electrolysis of water cannot be used without purification as it may contain some hydrogen. Combustible impurities may be removed by passage over copper oxide at 500 C.

5.7 *Pressure-Sensitive Tape*—Cellophane tape 1½ in. (38.1 mm) wide.[7]

5.8 *Sodium Hydroxide Solution (0.0725 N)*—Dissolve 2.9 g of sodium hydroxide (NaOH) in water and dilute to 1 liter. Standardize with potassium acid phthalate and adjust to 0.0725 N as described in Methods E 200.

6. Calibration Apparatus

6.1 *Calibration of Resistance Bridge*—The Mueller-type bridge should have its calibra-

tion checked at periodi
suitable external certifie

6.2 *Calibration of*
Thermometer—The pla
mometer is provided
constants determined
These are as follows:
the ice point; the funda
of the coil; and delta
formula. If the thermo
structed, the constants c
cantly change with time.
change slightly. Because
change and because R_0
with the Mueller bridge
value is given only to thr
should be determined in
the ice point[8] in duplica
days and averaging the r
checked periodically
months). If the value o
cantly (0.001 Ω), the cal
must be checked. If
changed a recalibration
ance thermometer is nece

7. Preparation of Appara

7.1 *Arrangement of A*
Install the platinum res
in the bucket so that at
of the sheath is immerse
cury-in-glass thermomete
halfway to the bottom of
the thermistor with its sen
the midpoint of the therm
these elements so that ex
is immersed each time th
Install a thermistor in t
the element immersed to
the bucket. It will be he
sary to have mercury-i
thermometers in both th
for quick temperature o
tors may be taped to the
the platinum resistance t
separately. If the thermi
thermometers, it should
manner that the sensing
midpoint of the thermon
mometer bulbs and ten

[3] See Jessup, R. S., "Precise Measurement of Heat of Combustion with a Bomb Calorimeter," *NBS Monograph* 7, U. S. Government Printing Office.

[4] "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, D.C. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, N.Y., and the "United States Pharmacopeia."

[5] *Annual Book of ASTM Standards*, Parts 20, 21, 22, 29, 31, 37, and 40.

[6] Obtainable from the National Bureau of Standards, Washington, D. C. 20234, as Standard Sample 39i.

[7] Scotch Brand cellophane tape No. 600, available from the Minnesota Mining and Manufacturing Co., has been found satisfactory for this purpose.

tion checked at periodic intervals against a suitable external certified resistance.

6.2 *Calibration of Platinum Resistance Thermometer*—The platinum resistance thermometer is provided with three calibration constants determined by the manufacturer. These are as follows: the resistance, R_0, at the ice point; the fundamental coefficient, c, of the coil; and delta (δ) in the Callendar formula. If the thermometer is properly constructed, the constants c and δ will not significantly change with time. The value of R_0 may change slightly. Because of this tendency to change and because R_0 should be determined with the Mueller bridge used in the test, this value is given only to three decimal places. R_0 should be determined initially by determining the ice point[8] in duplicate on three different days and averaging the results, and should be checked periodically (once every three months). If the value of R_0 changes significantly (0.001 Ω), the calibration of the bridge must be checked. If the bridge has not changed a recalibration of the platinum resistance thermometer is necessary.

7. Preparation of Apparatus

7.1 *Arrangement of Apparatus* (Note 4)—Install the platinum resistance thermometer in the bucket so that at least 6 in. (152 mm) of the sheath is immersed. Position the mercury-in-glass thermometer so that the bulb is halfway to the bottom of the bucket and locate the thermistor with its sensing element at about the midpoint of the thermometer bulb. Mount these elements so that exactly the same length is immersed each time the calorimeter is used. Install a thermistor in the water jacket with the element immersed to the same depth as in the bucket. It will be helpful, but not necessary to have mercury-in-glass calorimetric thermometers in both the bucket and jacket for quick temperature observations. Thermistors may be taped to these thermometers and the platinum resistance thermometer mounted separately. If the thermistors are taped to the thermometers, it should be done in such a manner that the sensing elements are at the midpoint of the thermometer bulbs. The thermometer bulbs and temperature-sensing elements must not touch the bomb, bucket, or water jacket (Note 5).

NOTE 4—This arrangement applies to the use of the Parr equipment for adiabatic measurements.

NOTE 5—If a Parr Series 1230 Adiabatic Calorimeter is used, then install the thermistor in the water jacket so that the sensing element is in direct line with the discharge stream from the pump.

7.2 *Calorimeter Controller and Heater*—Turn on the water heater and allow about 10 min for it to come to operating temperature. Assemble an oxygen bomb and place it in the calorimeter bucket with 2100 g of water. Place the bucket in the calorimeter jacket and close the cover. Start the calorimeter stirrer and controller. Lower the thermometers into place. Open the two throttling valves on the controller about one turn and add hot or cold water with the manual control until the galvanometer spot moves toward the center zero point. Allow the system to operate under automatic control and make adjustments with the throttling valves until the spot swings uniformly back and forth within not more than ten divisions on either side of the zero point. Use the mercury-in-glass thermometers and the balance control potentiometer to bring the bucket and jacket temperatures into balance, then using the platinum resistance thermometer adjust the balance control potentiometer so that the temperature of the bucket remains constant or lowers slightly (not more than 0.001 Ω in 5 min). The two valves (or plug-cocks) on the water inlet to the calorimeter shall be used for coarse adjustment when a full flow of hot or cold water is admitted to the jacket. The hot-water valve should be closed sufficiently to prevent an excessive temperature over-shoot during periods of rapid temperature rise. The cold-water valve should be closed far enough to prevent flooding when a full flow of cold water is admitted to the jacket.

8. Standardization

8.1 *Energy Equivalent of the Calorimeter*—Benzoic acid shall be used as the primary standard (Note 6). A sample weight should

[8] The ice point should be determined in accordance with the procedure described in "Notes to Supplement Resistance Thermometer Certificates," National Bureau of Standards (1949).

be chosen so that the temperature rise is approximately 0.32 Ω (3.2 C average temperature rise). Initially the energy equivalent should be determined by averaging six determinations made using benzoic acid over a period of at least 3 days. It should then be determined at frequent intervals using benzoic acid (every 1 or 2 days) with the average of the last six determinations being used for the energy equivalent. If any part of the equipment is changed or any part of the procedure is altered, the value should be redetermined. Make each determination in accordance with Section 9. Determine the correction for nitric acid (HNO_3) as described in 10.4 and substitute in the following equation:

$$W = (Q_b \times m + e_1)/\Delta t$$

where:

W = energy equivalent of calorimeter, cal/Ω, and
m = weight of benzoic acid, g, in vacuum (Note 7),
Δt = corrected temperature rise, as calculated in accordance with 10.2 or 10.3, Ω,
e_1 = correction for heat of formation of nitric acid, cal
Q_b = heat of combustion of benzoic acid, cal/g in vacuum calculated from the certified value in absolute kilojoules per gram mass (weight in vacuum) given for NBS Standard 39i. Multiply absolute kilojoules per gram mass (weight in vacuum) by 1000/4.1868 to obtain I.T. calories per gram in vacuum (Note 8).

NOTE 6—2,2,4-trimethyl pentane or *n*-dodecane, or both may be used for checking the energy equivalent of the system for use with volatile fuels.

NOTE 7—The value of m is determined as follows:

$$m = m_a + m_a [(D_a/D_s) - (D_a/D_w)]$$

where:

m_a = weight of benzoic acid in air, g,
m = weight of benzoic acid in vacuo, g,
D_s = density of benzoic acid = 1.320 g/cm³,
D_a = density of air, and
D_w = density of weights.

Since the air pressure, air humidity, and air temperature in the vicinity of the balance might vary within narrow limits for a specific laboratory, it may be possible to use an average value for D_a and thus establish a constant factor for the term $(D_a/D_s - D_a/D_w)$.

NOTE 8—The heat evolved by combustion of the standard sample should be multiplied by the following factor:*

$$1 + 10^{-6}[20(P - 30) + 42((m/V) - 3) + 30((M_w/V) - 3) - 45(t - 25)]$$

where:

P = initial absolute pressure of oxygen, atmospheres at temperature t,
m = weight of benzoic acid, g (in vacuum),
M_w = weight of water placed in bomb before combustion, g,
V = internal volume of bomb, liters, and
t = temperature to which the combustion reaction is referred, deg C (final temperature of the calorimeter).

8.2 *Heat of Combustion of Pressure-Sensitive Tape*—Determine the heat of combustion of the pressure-sensitive tape in accordance with Section 9 using about 1.2 g of tape and omitting the sample. Make at least three determinations and calculate the heat of combustion as follows:

$$Q_{pst} = (\Delta t \times W - e_1)/a$$

where:

Q_{pst} = heat of combustion of the pressure-sensitive tape, cal/g,
Δt = corrected temperature rise, as calculated in accordance with 10.2 or 10.3, Ω,
W = energy equivalent of the calorimeter, cal/Ω
e_1 = correction for the heat of formation of HNO_3, cal, and
a = weight of the pressure-sensitive tape, g.

Average the determinations, and redetermine the heat of combustion of the tape whenever a new roll is started.

9. Procedure

9.1 Turn on the water heater and the millimicrovoltmeter, if used. Make all electrical connections and open the water lines.

9.2 Before beginning, be sure that the bomb and its fittings are completely dry, inside and out.

9.3 Measure a piece of 36-gage (0.127-mm) platinum wire 100 mm long and attach the wire to the bomb electrodes forming a U-shaped loop.

9.4 Pipet 1.0 ml of water into the bomb and cover with a watch glass.

9.5 *Weight of Sample:*

9.5.1 Weigh the sample
semimicro analytical bal
pressure-sensitive tape
of the cup, trim arou
or blade, and seal tight
m strip of tape creased
aled by one edge in the
isk to give a flap arran
up and tape. Remove fro
orceps. Fill a hypoderm
ample. The volume of s
produce a temperature ris
0.32 Ω can be estimated as

$$V = (W \times 0.58)$$

where:

V = volume of sample to
W = energy equivalent c
cal/Ω,
Q = approximate heat of
sample, Btu/lb, and
D = specific gravity of th

NOTE 9—For relatively h
such as kerosine-type jet fuels
use tape.

9.5.2 Add the sample
serting the tip of the need
disk at a point so that th
cover the puncture upo
needle. Seal down the flap
with a metal spatula. Re
the tape and sample. C
throughout the weighing
to avoid contacting the ta
fingers. Place the cup in
and arrange the fuse wire
portion of the loop presses
of the tape disk.

9.6 *Bomb Assembly*—
and tighten the cover se
bomb to the oxygen cylinc
oxygen until a pressure o
Do not purge the bomb
air. Disconnect the bom
cylinder and replace the
Be careful not to overcha
accident, the oxygen intro
should exceed 40 atm, D
the combustion. A violer
of rupturing the bomb,
the filling connection and
the usual manner. Discar

*See *NBS Monograph 7*, p. 12.

9.5 *Weight of Sample:*

9.5.1 Weigh the sample cup to 0.01 mg on a semimicro analytical balance. Place a piece of pressure-sensitive tape (Note 9) across the top of the cup, trim around the edge with a razor blade, and seal tightly. Place a 3 by 12-mm strip of tape creased in the middle and sealed by one edge in the center of the tape disk to give a flap arrangement. Weigh the cup and tape. Remove from the balance with forceps. Fill a hypodermic syringe with the sample. The volume of sample necessary to produce a temperature rise of approximately 0.32 Ω can be estimated as follows:

$$V = (W \times 0.58)/(Q \times D)$$

where:

V = volume of sample to be used, ml,
W = energy equivalent of the calorimeter, cal/Ω,
Q = approximate heat of combustion of the sample, Btu/lb, and
D = specific gravity of the sample.

NOTE 9—For relatively high-boiling samples, such as kerosine-type jet fuels, it is not necessary to use tape.

9.5.2 Add the sample to the cup by inserting the tip of the needle through the tape disk at a point so that the flap of tape will cover the puncture upon removal of the needle. Seal down the flap by pressing lightly with a metal spatula. Reweigh the cup with the tape and sample. Care must be taken throughout the weighing and filling operation to avoid contacting the tape or cup with bare fingers. Place the cup in the curved electrode and arrange the fuse wire so that the central portion of the loop presses down on the center of the tape disk.

9.6 *Bomb Assembly*—Assemble the bomb and tighten the cover securely. Connect the bomb to the oxygen cylinder and slowly admit oxygen until a pressure of 30 atm is attained. Do not purge the bomb to remove entrapped air. Disconnect the bomb from the oxygen cylinder and replace the valve cover. **Caution:** Be careful not to overcharge the bomb. If by accident, the oxygen introduced into the bomb should exceed 40 atm, *DO NOT* proceed with the combustion. A violent explosion, capable of rupturing the bomb, might occur. Detach the filling connection and exhaust the bomb in the usual manner. Discard the sample.

NOTE 10—Pressures within the range of from 25 to 35 atm may be used, provided the same pressure is used for all tests, including standardization.

9.7 *Calorimeter Water:*

9.7.1 Adjust the temperature of the calorimeter water. The choice of the temperature to which the water is adjusted before weighing will depend on a number of factors, including room temperature, the desired initial temperature of the experiment, and the relative heat capacities of the calorimeter bucket, water, and bomb. No definite rule can be given, but the operator will learn by experience how to select the proper temperature under the conditions of his particular laboratory and apparatus. The following can be used as a guide:

Isothermal method	3.0 to 3.5 C below jacket temperature
Adiabatic method	1.5 to 1.8 C below room temperature

9.7.1.1 *Isothermal Method*—Adjust the temperature such that after assembly of the calorimeter bomb and bucket its temperature will be a few tenths of a degree below the desired initial temperature.

9.7.1.2 *Adiabatic Method*—Adjust the temperature so that the initial temperature of the determination will be as close to some fixed value as possible.

9.7.2 Weigh the calorimeter bucket to ±0.05 g on a heavy-duty analytical balance. After once establishing the dry bucket weight, it need only be checked occasionally. Fill with the desired quantity of water (2000 to 2100 g) and reweigh to 0.05 g (Note 11). The exact quantity of water is not important as long as it is enough to cover the bomb and its fittings and is the same in each determination.

NOTE 11—The change in weight of the water in the calorimeter bucket due to evaporation after weighing will affect the energy equivalent. The effect of this loss is small and will cancel if the procedure of placing the bomb in its bucket and completing the assembly of the system is carried out in the same manner and in the same length of time in the calibration experiments as in the measurement of the heat of combustion.

9.7.3 Immediately after weighing, place the bucket in position in the calorimeter jacket, carefully place the bomb in the bucket, and complete the firing circuit. Close the calorimeter cover and lower thermometers and thermistors.

NOTE 12—The bomb should be lowered into the

calorimeter without touching the water with the fingers. This can be done by using a hook on which the bomb can be hung and which can be removed after the bomb is in place in the calorimeter bucket. A hook made of a piece of brass rod about 1/16 in. (1.6 mm) in diameter has been found satisfactory. The hooked ends of the rod are inserted into holes on opposite sides of the screw top of the bomb and are easily removed after the bomb is in place.

9.8 *Procedure for Isothermal Method:*

9.8.1 Start the stirrer motor and the controller on the jacket heater to bring the temperature of the water in the jacket to 28 C. Take time and temperature readings over a 25-min period. During this period there are three definite time intervals:

9.8.1.1 An initial period of about 6 to 9 min during which the temperature change results solely from thermal leakage and heat of stirring.

9.8.1.2 A middle period of about 12 min, at the beginning of which the charge in the bomb is fired, and during which the temperature change is due primarily to the heat liberated by the combustion reaction in the bomb and partly to thermal leakage and heat of stirring, and

9.8.1.3 A final period of 9 to 11 min during which the temperature change is again due solely to thermal leakage and heat of stirring.

9.8.2 Allow the temperature of the calorimeter water to drift up to the starting temperature and then make and record readings of the time and temperature of the initial period. During this initial period when the rate of temperature rise is constant, make observations of temperature at 1-min intervals. The starting temperature always has the same value as determined from the calibration runs and is so chosen that the final temperature of the calorimeter after the combustion will be a few hundredths of a degree Celsius below the jacket temperature.

9.8.3 When the firing temperature is reached, fire the sample by closing the firing circuit through the fuse wire in the bomb by depressing the button on the ignition unit. The pilot light should glow momentarily and the temperature should start increasing in about 15 s. If the circuit does not close, or if it remains closed, or if the temperature does not start rising, the experiment has misfired and must be discontinued. After the combustion of the sample and during the middle period when the temperature is rising rapidly, make temperature observations first by setting the bridge dials successively at certain predetermined points (as determined during the standardization runs) and observing the times at which the galvanometer deflections become zero. After about 3 min, the rate of temperature rise will decrease so that temperature readings may be taken with more accuracy. These readings shall be continued until the rate of temperature change has been constant for at least 10 min. The readings made after the rate of temperature change has become constant constitute the final period.

NOTE 13—During the initial and final periods the resistance of the thermometer should be measured with the highest possible accuracy, since the over-all accuracy of the determination depends directly upon the accuracy of these temperature measurements. During the middle period, because of the very rapid rate of temperature rise, it is not possible to make readings as accurately as during the initial and final periods. This lack of accuracy is not important because the readings of the middle period are used only for calculating the relatively small correction for thermal leakage and heat of stirring.

9.9 *Procedure for Adiabatic Method:*

9.9.1 Start the stirrer motor and turn on the calorimeter controller. Use the manual control switch of the controller to bring the jacket temperature in close agreement with the bucket temperature. Allow the controller to automatically control the temperature and wait 15 min for equilibrium to be attained. At this point, and at the end point also, the temperature of the jacket should be controlled to the same temperature as the bucket, or slightly (0.005 C at most) below. Make readings at 1-min intervals until three consecutive readings show no change. Fire the sample by depressing the button of the ignition unit. The pilot light should glow momentarily and the temperature should start increasing in about 15 s. If the temperature does not start rising, the experiment has misfired and must be discontinued. Read and record the initial resistance, estimating the value to the nearest 0.00005 Ω.

9.9.2 After 6 min from firing, begin reading the resistance every minute. Continue until three consecutive readings show no change, or the readings decrease. Read and record the final resistance reading estimating the value to the nearest 0.00005 Ω.

9.10 *Analysis of Bomb Contents:*

9.10.1 Turn off the cont
and remove the bomb from
Open the needle valve and
escape at a rate such as to
to atmospheric in not less
the bomb and examine th
burned carbon. If any
carbon is found, the experi
jected. Wash the interior
cluding the electrodes and
with a fine jet of water
collect the washings in a
flask. Use a minimum amo
preferably less than 300 ml
ings with 0.0725 *N* NaO
methyl red indicator.

9.10.2 Determine the su
sample if it exceeds 0.05
ance with ASTM Method
Sulfur in Petroleum Prod
Method.[10]

10. Calculations

10.1 *Temperature R*
Method—Using data obta
plot a graph of readings of
time and calculate the co
rise, Δt, in ohms as follow

$$\Delta t = t_f - t_i - r_1 (b -$$

where:

Δt = corrected temperat
a = time of firing,
b = time (to nearest
temperature rise r
total (obtained gr
cally),
c = time at beginning
which the rate of
with time has beco
t_i = temperature at tim
t_f = temperature at tim
r_1 = rate at which th
rising during the
firing, Ω, and
r_2 = rate at which the te
during the final pe

10.2 *Temperature Ris*
—Using data obtained i
the temperature rise, Δt,

$$\Delta t = t_f$$

where:

Δt = corrected temperat

9.10.1 Turn off the controller and stirrer and remove the bomb from the calorimeter. Open the needle valve and allow the gas to escape at a rate such as to reduce the pressure to atmospheric in not less than 1 min. Open the bomb and examine the interior for unburned carbon. If any trace of unburned carbon is found, the experiment should be rejected. Wash the interior of the bomb including the electrodes and the sample cup with a fine jet of water and quantitatively collect the washings in a 500-ml Erlenmeyer flask. Use a minimum amount of wash water, preferably less than 300 ml. Titrate the washings with 0.0725 *N* NaOH solution using methyl red indicator.

9.10.2 Determine the sulfur content of the sample if it exceeds 0.05 percent in accordance with ASTM Method D 129, Test for Sulfur in Petroleum Products by the Bomb Method.[10]

10. Calculations

10.1 *Temperature Rise, Isothermal Method*—Using data obtained in Section 9, plot a graph of readings of temperature versus time and calculate the corrected temperature rise, Δt, in ohms as follows:

$$\Delta t = t_f - t_i - r_1 (b - a) - r_2 (c - b)$$

where:

Δt = corrected temperature rise, Ω,
a = time of firing,
b = time (to nearest 0.1 min) when the temperature rise reaches 63 percent of total (obtained graphically or numerically),
c = time at beginning of final period in which the rate of temperature change with time has become constant,
t_i = temperature at time of firing, Ω,
t_f = temperature at time c, in Ω,
r_1 = rate at which the temperature was rising during the initial period before firing, Ω, and
r_2 = rate at which the temperature was rising during the final period, Ω.

10.2 *Temperature Rise, Adiabatic Method*—Using data obtained in Section 9, calculate the temperature rise, Δt, in ohms, as follows:

$$\Delta t = t_f - t_i$$

where:

Δt = corrected temperature rise, Ω,
t_f = final equilibrium temperature, Ω, and
t_i = temperature at time of firing, Ω.

10.3 *Thermochemical Corrections (Appendix A2)*—Calculate the following corrections for each test:

e_1 = correction for the heat of formation of the HNO_3, cal = milliliters of standard (0.0725 *N*) NaOH solution used in titration.
e_2 = correction for the heat of formation of sulfuric acid (H_2SO_4), cal = 14 × percentage of sulfur in sample × weight of sample, g.
e_3 = correction for the heat of combustion of pressure-sensitive tape, cal = weight of tape, g × heat of combustion of tape cal/g.

10.4 *Gross Heat of Combustion*—Calculate the gross heat of combustion by substituting in the following equations:

$$Q_g \text{ (gross, } t \text{ C)} = (\Delta t \times W - e_1 - e_2 - e_3)/M \times 1.8 \text{ Btu/lb}$$

$$Q_g \text{ (gross, 25 C)} = (\Delta t \times W - e_1 - e_2 - e_3)/M \text{ cal/g}$$

$$Q_g \text{ (gross, 25 C)} = Q_g \text{ (gross, } t \text{ C)} + A\ (t - 25) \text{ Btu/lb}$$

where:

Q_g (gross, t C) = gross heat of combustion at constant volume expressed as cal/g or Btu/lb,
Q_g (gross, 25 C) gross heat of combustion at constant volume expressed as Btu/lb,
Δt = corrected temperature rise, Ω,
W = energy equivalent of calorimeter, cal/Ω,
M = weight of sample in air, g,
t = final temperature of combustion, deg C,
e_1, e_2, e_3 = corrections as described in 10.3, and
A = correction factor, Btu/lb·deg C to correct from final temperature of combustion to 25 C[11] where values of factor A are given in Table 1.

10.5 *Net Heat of Combustion*—Calculate the net heat of combustion as follows:

$$Q_n \text{ (net, 25 C)} = Q_g \text{ (gross, 25 C)} - 91.23 \times H$$

where:

Q_n (net, 25 C) = net heat of combustion at

[10] *Annual Book of ASTM Standards*, Part 23.
[11] See *NBS Monograph 7*, p. 16.

constant pressure, Btu/lb (weight in air),

Q_g (gross, 25 C) = gross heat of combustion at constant volume, Btu/lb (weight in air), and

H = weight percent of hydrogen in the sample.

If the percentage of hydrogen in the sample is not known, determine the hydrogen in accordance with ASTM Method D 1018, Test for Hydrogen in Petroleum Fractions.[10]

11. Report

11.1 Net heat of combustion is the quantity required in practical applications. Both gross and net heat should be reported to the nearest Btu per pound.

12. Precision

12.1 The following criteria should be used for judging the acceptability of results (95 percent confidence):

12.1.1 *Repeatability*—Duplicate results by the same operator should be considered suspect if they differ by more than the following amounts:

	Gross Heat of Combustion, Btu/lb	Net Heat of Combustion,[a] Btu/lb
Jet fuel	20	22
Aviation gasoline	29	31

[a] Calculated values based on precision of hydrogen determination in accordance with Method D 1018.

12.1.2 *Reproducibility*—The results submitted by each of two laboratories should be considered suspect if they differ by more than the following amounts:

	Gross Heat of Combustion, Btu/lb	Net Heat of Combustion[a] Btu/lb
Jet fuel	53	56
Aviation gasoline	119	120

[a] Calculated values based on precision of hydrogen determination in accordance with Method D 1018.

TABLE 1 Values of Factor A

Qg (Gross, t C)	A	Qg (Gross, t C)	A
Btu/lb	Btu/lb·deg C	Btu/lb	Btu/lb·deg C
18 500	0.68	19 600	1.14
18 600	0.72	19 700	1.18
18 700	0.76	19 800	1.22
18 800	0.80	19 900	1.26
18 900	0.85	20 000	1.30
19 000	0.89	20 100	1.35
19 100	0.93	20 200	1.39
19 200	0.97	20 300	1.43
19 300	1.01	20 400	1.47
19 400	1.05	20 500	1.51
19 500	1.09	20 600	1.55

A1. APPA

A1.1 Test Room

A1.1.1 The room in which the ated must be free from drafts sudden temperature changes. Th is not important as long as it is 7s F (23 to 26 C) and is held con ture must be constant, not only out from one time of the year to rays of the sun shall not strike the bridge, and galvanometer. Ade lighting, heating, and ventilation Thermostatic control of room te trolled humidity are desirable.

A1.2 Oxygen Bomb

A1.2.1 The oxygen bomb sha volume of 350 ± 50 ml. All parts of materials that are not affected process or products sufficient to able heat input or alteration of e bomb is lined with platinum or shall be sealed to prevent combus reaching the base metal. The bom so that all liquid combustion pr pletely recovered by washing t There must be no gas leakage bomb must be capable of withsta pressure test to 3000 psig (20.7 room temperature without stressi its elastic limit.[12] If necessary, m that the feet are 12 mm high to all circulation under the bomb.

A1.3 Calorimeter Bucket

A1.3.1 The calorimeter bucke metal (preferably copper or brass sistant coating, and with all ou polished. Its size shall be such th completely immersed in water wh is assembled. It shall have a dev water thoroughly and at a uniform imum heat input. Continuous s shall not raise the temperature starting with identical temperatu ter, room, and jacket. The imme stirrer shall be coupled to the out lenal of a low heat conductivity.

A1.4 Jacket

A1.4.1 The calorimeter bomb shall be completely enclosed wi jacket and supported so that its tom are approximately 1 cm fro The jacket may be arranged so as stant temperature, or with provi

ator should be considered sus-
ffer by more than the following

Gross Heat of Combustion, Btu/lb	Net Heat of Combustion,[a] Btu/lb
20	22
29	31

ues based on precision of hydrogen de-
cordance with Method D 1018.

oducibility—The results sub-
of two laboratories should be
spect if they differ by more than
mounts:

Gross Heat of Combustion, Btu/lb	Net Heat of Combustion[a] Btu/lb
53	56
119	120

es based on precision of hydrogen de-
rdance with Method D 1018.

deg C

14
8
2
6
30
5
9
3
27
1
5

APPENDIXES

A1. APPARATUS FOR HEAT OF COMBUSTION TEST

A1.1 Test Room

A1.1.1 The room in which the calorimeter is operated must be free from drafts and not subject to sudden temperature changes. The exact temperature is not important as long as it is in the range of 74 to 78 F (23 to 26 C) and is held constant. The temperature must be constant, not only throughout the day, but from one time of the year to another. The direct rays of the sun shall not strike the calorimeter jacket, bridge, and galvanometer. Adequate facilities for lighting, heating, and ventilation should be provided. Thermostatic control of room temperature and controlled humidity are desirable.

A1.2 Oxygen Bomb

A1.2.1 The oxygen bomb shall have an internal volume of 350 ± 50 ml. All parts shall be constructed of materials that are not affected by the combustion process or products sufficient to introduce measurable heat input or alteration of end products. If the bomb is lined with platinum or gold, all openings shall be sealed to prevent combustion products from reaching the base metal. The bomb must be designed so that all liquid combustion products can be completely recovered by washing the inner surfaces. There must be no gas leakage during a test. The bomb must be capable of withstanding a hydrostatic pressure test to 3000 psig (20.7 MN/m^2, gage) at room temperature without stressing any part beyond its elastic limit.[12] If necessary, modify the bomb such that the feet are 12 mm high to allow for better water circulation under the bomb.

A1.3 Calorimeter Bucket

A1.3.1 The calorimeter bucket shall be made of metal (preferably copper or brass) with a tarnish-resistant coating, and with all outer surfaces highly polished. Its size shall be such that the bomb will be completely immersed in water when the calorimeter is assembled. It shall have a device for stirring the water thoroughly and at a uniform rate but with minimum heat input. Continuous stirring for 10 min shall not raise the temperature more than 0.01 C starting with identical temperatures in the calorimeter, room, and jacket. The immersed portion of the stirrer shall be coupled to the outside through a material of a low heat conductivity.

A1.4 Jacket

A1.4.1 The calorimeter bomb, bucket, and water shall be completely enclosed within a stirred water jacket and supported so that its sides, top, and bottom are approximately 1 cm from the jacket walls. The jacket may be arranged so as to remain at a constant temperature, or with provisions for automatically adjusting the jacket temperature to equal that of the calorimeter bomb, bucket, and water for adiabatic operation. It must be constructed so that any water evaporating from the jacket will not condense on the calorimeter bucket.[13]

A1.5 Thermometers

A1.5.1 Temperatures in the jacket and the calorimeter, respectively, shall be measured with the following thermometers:

A1.5.1.1 *Etched Stem, Mercury-in-Glass, ASTM Bomb Calorimeter Thermometers*, having a range from 66 to 95 F, 19 to 35 C, 18.9 to 25.1 C, or 23.9 to 30.1 C as specified, and conforming to the requirements for Thermometer 56F, 56C, 116C, or 117C, respectively, as prescribed in ASTM Specification E 1, for ASTM Thermometers.[14] Each of these thermometers shall have been tested for accuracy at intervals no larger than 2.5 F or 1.5 C over the entire graduated scale. Corrections shall be reported to 0.005 F or 0.002 C, respectively, for each test point.

A1.5.1.2 *Platinum Resistance Thermometer*—A 25-Ω calorimetric-type platinum resistance thermometer, calibrated by the National Bureau of Standards or by the supplier, should be used. The thermometer should be enclosed in a metal sheath.[15]

A1.6 Resistance Bridge

A1.6.1 A Wheatstone-type bridge capable of measuring resistance to 0.0001 Ω is required.[16]

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[12] The oxygen bomb (Parr No. 1101 or equivalent) must meet the requirements specified in ASTM Recommended Practice E 144, for Safe Use of Oxygen Combustion Bombs, *Annual Book of ASTM Standards*, Part 41.

[13] The following calorimeter jackets have been found adequate:

For isothermal operation:

Precision Scientific Co. No. 63090 calorimeter.

Parr Instrument Co. No. 1230 calorimeter with No. 2651 controller.

For adiabatic operation:

Parr Instrument Co. Series 1210, 1220, or 1230 calorimeters with 2601 controller, provided that Series 1210 and 1220 jacket covers are properly fitted with an additional opening for the platinum resistance thermometer and a suitable device for raising and lowering it.

[14] *Annual Book of ASTM Standards*, Parts 25 and 44.

[15] Metal-sheathed platinum resistance thermometer No. 8163-B available from Leeds & Northrup Co., 4901 Stenton Ave., Philadelphia, Pa. 19144, has been found satisfactory for this purpose.

[16] Bridge No. 8167 obtainable from Leeds & Northrup Co., or equivalent, has been found satisfactory for this purpose.

A1.7 Null Point Indicators

A1.7.1 Either a galvanometer or millimicrovoltmeter may be used.

A1.7.1.1 *Galvanometer and Accessories*—A galvanometer having a sensitivity of 0.2 μV/mm at 1 m is required. The galvanometer may be supported by a Julius suspension if necessary to reduce the effect of vibrations. Any suitable lamp and scale device may be used in reading the galvanometer.[17]

A1.7.1.2 *Millimicrovoltmeter.*[18]

A1.8 Timing Device

A1.8.1 A watch or other timing device capable of measuring time to 1 s is required for use with the isothermal method.

A1.9 Sample Cup

A1.9.1 A low-form platinum cup, 26 mm in diameter and 11 mm deep with a spun rim.[19]

A1.10 Firing Circuit

A1.10.1 A 6 to 16-V alternating or direct current is required for ignition purposes with an ammeter or pilot light in the circuit to indicate when current is flowing. A step-down transformer connected to a 115 V, 50/60-Hz lighting circuit or storage battery may be used.[20]

NOTE 14: **Caution**—The ignition circuit switch shall be of the momentary contact type, normally open, except when held closed by the operator.

[17] The following apparatus have been found satisfactory for this purpose:
Galvanometer, Leeds and Northrup No. 2284.
Julius Suspension, Leeds and Northrup No. 2162.
Lamp and Scale, Leeds and Northrup No. 2100.

[18] Model No. 149 manufactured by the Keithley Instrument Co., 12415 Euclid Ave., Cleveland, Ohio 44106, or any instrument of equivalent sensitivity is satisfactory.

[19] Parr No. 43A 6 sample cup has been found satisfactory for this purpose.

[20] Parr No. 2900 transformer has been found satisfactory for this purpose.

A2. CORRECTIONS

A2.1 Thermometer Corrections

A2.1.1 It is not necessary to apply stem corrections to the thermometers as the platinum resistance thermometer makes the precise readings of temperature.

A2.2 Thermochemical Corrections

A2.1.2 *Heat of Formation of Nitric Acid*—A correction of 1 cal is applied for each milliliter of standard (0.0725 *N*) NaOH solution used in the acid titration. This is based on the assumption that (*1*) all of the acid titrated is HNO_3 and (*2*) the heat of formation of 0.1 *N* KNO_3 under the test conditions is 13.8 kcal/mole. When H_2SO_4 is also present, part of the correction for H_2SO_4 is contained in the e_1 correction, and the remainder in the e_2 correction.

A2.1.2 *Heat of Formation of Sulfuric Acid*—A correction of 1.4 kcal is applied for each gram of sulfur in the sample. This is based upon the heat of formation of 0.17 *N* H_2SO_4, which is −72 kcal/mole. But, a correction equal to 2 × 13.8 kcal/mole of sulfur was applied for H_2SO_4 in the e_1 correction. Thus, the additional correction necessary is 72 − (2 × 13.8) = 44.4 kcal/mole or 1.4 kcal/g of sulfur.

The value of 1.4 kcal/g of sulfur is based on a fuel oil containing a relatively large amount of sulfur since as the percentage of sulfur decreases, the correction decreases and consequently a larger error can be tolerated. For this calculation 0.8 percent S, 99.2 percent CH_2 was taken as the empirical composition of fuel oil. If a 0.6-g sample of such a fuel oil is burned in a bomb containing 1 ml of water, the H_2SO_4 formed will be approximately 0.17 *N*. Using data from National Bureau of Standards *Circular No. 500*, the heat of reaction SO_2 (g) + $\frac{1}{2}$ O_2 (g) + 651 H_2O (l) = $H_2SO_4 \cdot 650\ H_2O$ (l) at constant volume and 30 atm is −72 kg-cal/mole.

A2.1.3 *Heat of Combustion of Fuse Wire*—When using platinum wire no correction need be applied for the heat of combustion of the wire. The electrical energy required can be neglected if the same length of wire is used in both the energy equivalent and unknown experiments.

A2.1.4 *Heat of Combustion of Pressure-Sensitive Tape*—The correction for the heat of combustion of the tape (as determined in accordance with 7.2) assumes complete combustion of the tape.

A3. EXPERIMENTAL DATA

A3.1 Results of tests made by the high-precision calorimetry method are given in Table A1.

TABLE A1 Results Obtained by the High-Precision Calorimetry Method

	Laboratory										
	A	B	C	D	E	F	G	H	I	J	
Standardization of calorimeter energy equivalent cal/Ω	49 033	25 314	24 216	24 265	33 774	23 923	24 301	24 232	24 031	40 083	
	49 045	25 311	24 219	24 280	33 786	23 917	24 334	24 223	24 029	40 085	
	49 059	25 310	24 219	24 263	33 775	23 918	24 272	24 237	24 028	40 083	
Heat of combustion of tape cal/g	5 913	5 862	5 936	5 880	5 890	5 893	5 944	5 860	5 873	5 759	
	5 910	5 822	5 950	5 884	5 942	5 884	5 919	5 842	5 757	5 725	
	5 909	5 896	5 947	5 882	5 857	5 882	5 956	5 864	5 667	5 719	

TABLE A1 Results Obtained by the High-Precision Calorimetry Method[a]

	Laboratory									
	A	B	C	D	E	F	G	H	I	J
Standardization of calorimeter energy equivalent cal/g	49 033	25 314	24 216	24 285	33 774	23 923	24 301	24 232	24 031	40 083
	49 045	25 311	24 219	24 280	33 786	23 917	24 334	24 223	24 029	40 085
	49 059	25 310	24 219	24 283	33 775	23 918	24 272	24 237	24 028	40 083
Heat of combustion of tape cal/g	5 913	5 862	5 936	5 880	5 890	5 893	5 944	5 860	5 873	5 759
	5 910	5 822	5 950	5 884	5 942	5 884	5 919	5 842	5 757	5 725
	5 909	5 896	5 947	5 882	5 857	5 882	5 956	5 864	5 667	5 719
Heat of combustion of *isooctane*, Btu/lb (gross)	20 543	20 536	20 494	20 531	20 543	20 546	20 547	20 554	20 577	20 542
	20 548	20 544	20 527	20 525	20 533	20 534	20 525	20 525	20 576	20 544
	20 535	20 534	20 523	20 522	20 547	20 538	20 529	20 574	20 563	20 545
Heat of combustion of supersonic jet fuel, Btu/lb (gross)										
With tape	20 263	20 293	20 259	20 264	20 273	20 256	20 303	20 299	20 288	20 284
	20 258	20 293	20 252	20 248	20 270	20 257	20 327	20 302	20 284	20 281
Without tape	20 278	20 292	20 268	20 290	20 274	20 275	20 259	20 286	20 282	20 275
	20 263	20 290	20 264	20 286	20 263	20 273	20 264	20 288	20 281	20 275
Heat of combustion of conventional jet fuel, Btu/lb (gross)										
With tape	19 843	19 844	19 832	19 845	19 842	19 837	19 867	19 856	19 848	19 850
	19 830	19 839	19 831	19 854	19 848	19 828	19 852	19 843	19 862	19 848
Without tape	19 832	19 838	19 831	19 836	19 824	19 802	19 777	19 852	19 835	19 832
	19 838	19 839	19 832	19 832	19 814	19 834	19 782	19 850	19 834	19 827
Heat of combustion of aviation gasoline 100/130, Btu/lb (gross)	20 491	20 508	20 005[b]	20 504	20 512	...	20 540	20 560	20 593	20 552
	20 488	20 512	20 156[b]	20 495	20 501	...	20 518	20 569	20 590	20 553
Heat of combustion of aviation gasoline 115/145, Btu/lb (gross)	20 335	20 355	20 241[b]	20 340	20 301	...	20 286	20 295	20 392	20 357
	20 343	20 354	20 372[b]	20 342	20 317	...	20 290	20 336	20 402	20 365
Hydrogen content, wt percent supersonic jet fuel	15.12	15.11	15.19	15.48	15.12	...	14.63	15.12	15.13	...
	15.02	15.09	14.99	15.51	15.17	...	14.71	15.12	15.17	...
Conventional jet fuel	13.78	13.89	13.77	13.84	13.95	...	13.75	14.28	13.82	...
	13.91	13.89	13.63	13.88	13.98	...	13.80	14.21	13.87	...

[a] 1964 Cooperative program, Research Division XI.
[b] Not used in the statistical analysis.

TABLE A1 *Continued*

	Laboratory									
	A	B	C	D	E	F	G	H	I	J
Aviation gasoline 100/130	15.81	15.90	...	15.89	15.75	...	15.68	16.36	16.02	...
	15.85	15.88	...	15.83	15.58	...	15.58	16.42	16.00	...
Aviation gasoline 115/145	15.30	15.32	...	15.47	15.72	...	15.13	15.64	15.39	...
	15.28	15.28	...	15.43	15.46	...	15.16	15.64	15.41	...
API gravity at 60 F:										
Supersonic jet fuel	52.6	52.4	52.3	52.6	52.9	...	52.8	52.6	52.3	...
Conventional jet fuel	44.0	43.7	43.7	45.6	44.1	...	44.0	44.1	43.7	...
Aviation gasoline 100/130	72.7	72.6	72.3	72.5	71.8	...	72.6	72.6	72.5	...
Aviation gasoline 115/145	68.8	68.7	68.4	69.0	68.6	...	68.9	68.7	68.6	...
Aniline point, deg F:										
Supersonic jet fuel	180.8	180	181.2	181.0	179.9	...	180.7	180.0	180.3	...
Conventional jet fuel	141.6	140	142.9	141.5	141.4	...	141.8	142.5	141.4	...
Aviation gasoline 100/130	164.3	163	164.5	164.0	164.3	...	162.8	126.0	164.3	...
Aviation gasoline 115/145	151.0	151	151.9	151.5	150.1	...	150.4	134.0	150.6	...
Sulfur content, wt percent:										
Supersonic jet fuel	0.003	0.003	0.004	0.0001	...	0.00	0.00	0.030	0.0001	...
Conventional jet fuel	0.022	0.026	0.026	0.030	0.0558	0.02	0.025	0.080	0.0230	...
Aviation gasoline 100/130	0.003	0.012	0.003	0.0005	0.0574	...	0.007	0.049	0.0015	...
Aviation gasoline 115/145	0.002	0.013	0.003	0.0002	...	...	0.006	0.045	0.0020	...
Average weight of tape disk	0.0573	0.048	0.053	...	...	0.0465	...	0.0497	...	...
Type of calorimeter	Isothermal	Adiabatic	Adiabatic	Adiabatic	Isothermal	Adiabatic	Adiabatic	Adiabatic	Adiabatic	Isothermal
Type of null indicator	Galvanometer	Galvanometer	Electric detector	Millimicrovolumeter	Galvanometer	Galvanometer	Galvanometer	Galvanometer	MMVM	Galvanometer
Automatic temperature controller	yes	yes	yes	yes	yes	yes	yes	yes	yes	...
ASTM Method for sulfur	D 1266	D 1266	D 1266	...	D 129	D 129	D 1266	D 1266	D 1266	...
Method of hydrogen determination	Rapid combustion	ASTM D 1018	Semimicrocombustion	Beta-ray	Microcombustion	...	Microcombustion	Beta-ray	...	...

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Standard Methods o
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This Standard is issued under the fixed desi
the year of original adoption or, in the case
year of last reapproval.

1. Scope

1.1 These methods cover the de
of the total volatile organic chlor
centrations from 10 to 100 ppm
butene mixtures. The amperomet
not directly applicable in the prese
substances that combine with s
oxidize chloride ion in dilute ac
Bromides, sulfides, ammonia, tob
and more than 25 μg of hydroge
the test solution interfere in the
tometric procedure.

1.2 Dissolved sodium chloride
titatively determined using these

2. Summary of Methods

2.1 *Combustion Methods*—E
or oxy-hydrogen method may
combustion.

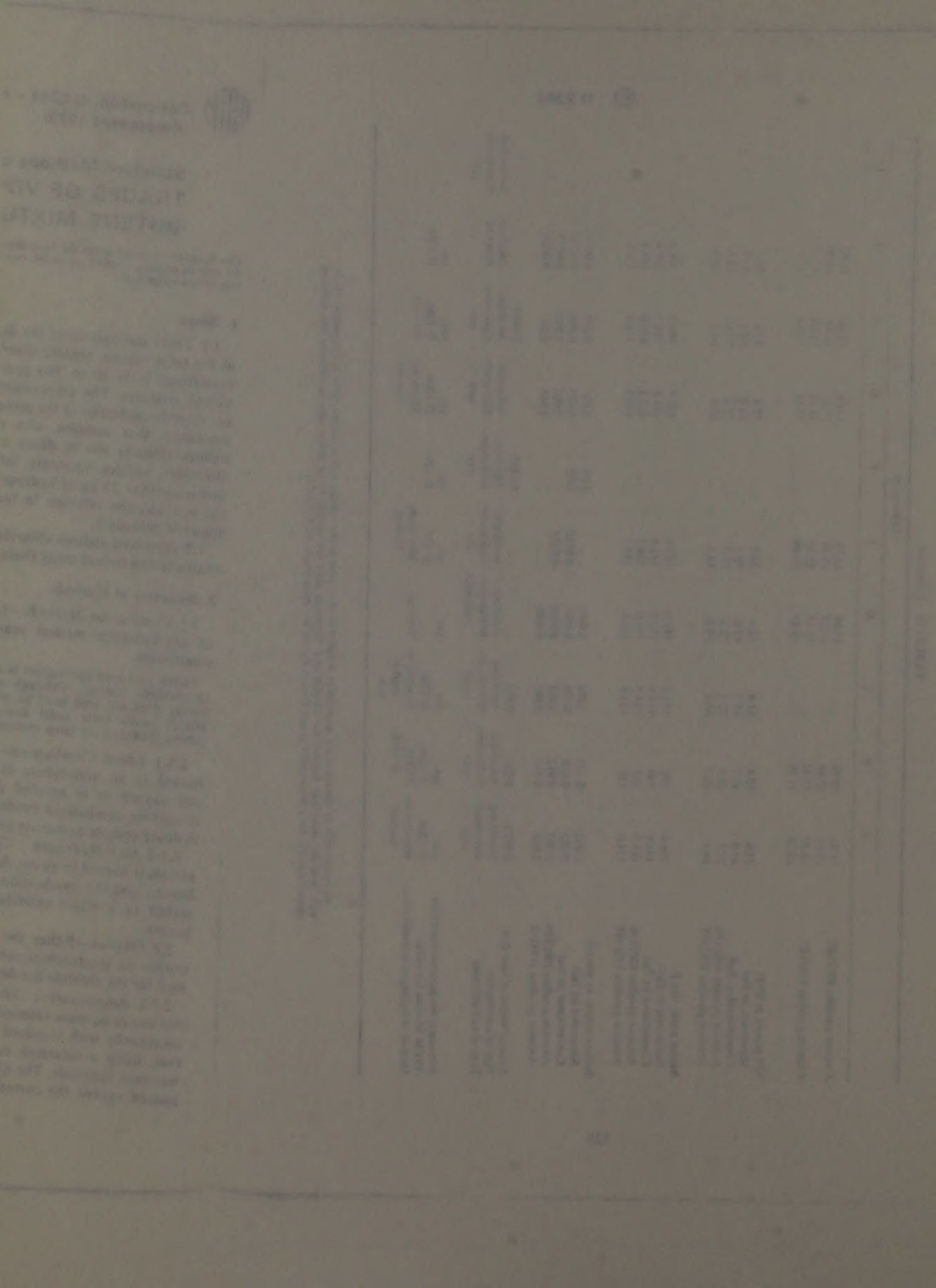
NOTE 1—Lamp combustion is r
to multiple testing. Although a
burner does not lend itself to m
affords much more rapid analy
sample than does the lamp combus

2.1.1 *Lamp Combustion*—
burned in an atmosphere of
and oxygen or in purified a
containing combustion produc
in dilute sodium carbonate sol

2.1.2 *Oxy-Hydrogen Co*
sample is burned in an oxy-hy
burner, and the combustion
sorbed in a dilute solution
bonate.

2.2 *Finishes*—Either the
tration or spectrophotometr
used for the chloride ion dete

2.2.1 *Amperometric Titr*
ride ion in aqueous solution
ometrically with standard
tion, using a saturated cal
reference electrode. The dif
plotted against the corresp



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Calculating heating values from elemental compositions of fossil fuels

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(Received 5 May 1978)

Heating value and elemental composition of fossil fuels are important parameters for judging the quality of the fuel substances. Often in an analytical laboratory, both the heating value and the elemental composition are measured for the same sample. Newer instrumentation (gas-chromatographic elemental analysers, X-ray fluorescence, induction furnace) has made elemental analyses quick, routine and precise. For example, C, H, and N can be determined in less than 15 min using such instrumentation. Heating-value measurements take up to 30 min per sample and require lengthy set-up and calculation procedures. Therefore, a formula which accurately calculates heating values based upon elemental composition could be valuable to the work of the analytical chemist. The purpose of this communication is to show that such a formula does exist and that it is applicable to a wide variety of fossil fuel substances.

The formula to which we refer, developed by Boie[1], has the form:

$$H_g(\text{cal/g}) = 8400C + 27\,765H + 1500N + 2500S - 2650O \qquad (1)$$

where H_g is the gross heating value and C, H, N, S, and O are the normalized weight fractions of these elements in the sample. Multiplication by the factor 1.8 converts the results to units of Btu/lb and by 4.187 to J/g.

We have applied the Boie equation to a large number of fossil fuel substances. The results of these calculations are compared with determined values in *Table 1*. To complete the evaluation, we also calculated heating values using the well-known Dulong equation:

$$H_g(\text{Btu/lb}) = 14\,544C + 62\,028(H - O/8) + 4050S \qquad (2)$$

The Dulong equation assumes that all the oxygen is associated with hydrogen to form water, with the excess hydrogen available for combustion[2].

The average percent differences in *Table 1* were obtained by taking the difference between the calculated and measured values, dividing this by the measured value, multiplying this number by 100 to obtain a percent difference, and

Table 1 Comparison of measured and calculated heating values

Type of sample	No. of samples	Average difference (%)	
		Boie eq.	Dulong eq.
Liquid fuel oils	200	1.58	5.61
Wyoming coals[5]	54	1.86	1.41
Foreign shale oils[1]	28	0.94	3.57
Crude oil residuums[6]	18	0.33 (C, H only)	4.54

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averaging the percent differences over the number of samples in the set. The measured values are those obtained following prescribed bomb-calorimetric procedures[3].

The liquid fuel oils in *Table 1* were mostly shale oils obtained from various above-ground, *in situ*, and experimental laboratory retorting processes. A small number of tar sand bitumen and coal tar samples are also included in this set. The foreign shale oils were derived from a set of oil shales representing a spectrum of geologic age, environment, source material, and elemental composition. These oil shales had been previously analysed, chemically and petrographically[4]. The coal samples, taken from active mines in four of the ten major coal-bearing areas of Wyoming, represent 32 different coals ranging in age from Upper Cretaceous to Eocene. These, too, have been previously analysed[5]. The crude oil residuums included one from Kentucky, two from California, and three Midcontinent crude oils. Each of these was further partitioned into a cracking stock and a normal and flashed residuum[2].

The results in *Table 1* clearly show that overall the Boie equation is far superior to the Dulong equation for calculating heating values from elemental compositions. Only in the case of coals does the Dulong equation provide better results, and then, not significantly better. In general,

Table 2 Data for heating-value calculations using Boie equation for foreign shale oils[4]

Sample	(wt %)					Btu/lb		
	C	H	N	S	O	Meas.	Calc.	Diff. (%)
Australia								
1	84.6_4	11.5_0	0.56	0.30	3.0_0	18800	18430	1.97
2	84.4_4	11.9_8	0.57	0.43	2.6_2	19000	18660	1.79
3	85.1_8	11.8_4	0.56	0.42	2.0_0	18980	18740	1.26
4	85.5_6	12.0_2	0.52	0.39	1.5_1	19080	18900	0.94
5	85.3_0	12.0_0	0.54	0.44	1.6_3	18950	18870	0.42
6	84.3_-	12.0_4	0.48	0.48	2.6_3	19020	18680	1.79
7	85.5_6	10.5_7	0.72	0.62	2.5_3	18200	18150	0.27
Brazil								
8	83.3_2	11.7_3	0.97	0.24	3.7_9	18860	18320	2.86
9	84.2_8	12.0_5	1.10	0.25	2.3_2	18900	18700	1.06
10	85.6_6	11.5_3	–	0.60	2.2_1	18610	18640	0.16
11	85.1_5	12.0_2	–	0.43	2.4_0	18830	18790	0.20
12	85.0_8	12.4_4	–	0.38	2.1_0	19030	19000	0.16
France								
13	84.8_8	11.3_6	0.84	0.31	2.6_1	18670	18420	1.34
14	85.0_7	11.4_3	1.12	0.32	2.0_6	18580	18520	0.32
15	84.5_6	11.2_8	1.18	0.35	2.6_3	18540	18350	1.02
16	85.2_4	11.5_8	1.00	0.21	1.6_7	18920	18780	0.74
17	83.7_4	10.5_4	0.66	2.76	2.3_0	18260	17960	1.64
18	85.1_6	11.2_6	0.59	0.46	2.5_3	18580	18420	0.86
Manchuria								
19	81.2_4	11.9_1	0.84	0.19	5.8_2	18240	17990	1.37
New Zealand								
20	83.3_5	11.8_0	0.60	0.64	3.6_1	18640	18370	1.45
Sweden								
21	84.9_5	9.0_0	0.71	1.72	3.6_1	17460	17270	1.09
22	85.8_7	9.7_6	0.72	1.32	2.3_3	17980	17830	0.83
Thailand								
23	84.4_2	12.4_4	1.10	0.41	1.6_3	18920	18950	0.16
South Africa								
24	84.9_8	10.8_2	–	0.67	3.5_3	17980	18120	0.78
25	84.8_4	11.1_3	–	0.64	3.3_9	18150	18260	0.61
26	84.9_9	11.1_1	–	0.63	3.2_7	18190	18280	0.49
27	85.1_3	11.4_6	–	0.59	2.8_2	18370	18490	0.65
28	84.9_9	11.5_5	–	0.53	2.9_3	18540	18510	0.16

Table 3 Compositional data and calculated heating values for the organic matter in Green River and New Albany Formation oil shales

Sample	(wt %)					Calculated heating value (Btu/lb)	
	C	H	N	S	O	Complete eq.	C, H terms
Green River Formation[8]	80.5	10.3	2.4	1.0	5.8	17150	17320
New Albany Formation[7]	82.0	7.4	2.3	2.0	6.3	16100	15950

N, S, and O make up a small portion of the total organic content of fuel oil. Often, the contributions from the N and S contents, coupled through their coefficients in the Boie equation, are cancelled by the O contribution. Thus, the bulk of the heating value is due overwhelmingly to the C and H contributions. The calculated heating values for the crude oil residuums in *Table 1* were obtained in this manner. That is, only the C, H terms of the Boie equation were used. Complete elemental analyses were not reported for these residuums. It is indeed remarkable that these two terms provide such a close approximation to the gross heating value of a crude oil substance.

In *Table 2* we present the raw data and calculated heating values for the foreign shale oils. These data illustrate typical results obtained using the Boie equation.

Measured heating values of raw oil shales are questionable because of interferences caused by minerals which add to or subtract from the true value. Even a 'rich' oil shale yielding 30–35 U.S. gal/ton (125–146 l/t) would contain about 85% mineral matter. However, valid estimates of the heating values of the organic matter in raw shales can still be made using the Boie equation and by determining the composition of the organic matter in the formation. This is done by preparing organic concentrates of raw shales and determining the elemental composition of the concentrated material. Smith and Young[7] have done this for the New Albany oil shales of Kentucky. Smith[8] has also determined the ultimate composition of the organic matter in Green River Formation oil shale. These data are shown in *Table 3* along with heating values calculated from the complete Boie equation and heating values calculated with only the C, H terms. The data show that contributions to the heating value from N, S, and O combine to yield less than 1% of the total, and usually can be neglected. Therefore, good estimates of the heating values of raw shales can be obtained using only the C, H terms. However, the analysis of carbon is the only one which is directly relatable to the organic material. Hydrogen determinations in oil shales include organic as well as inorganic contributions. Using the organic carbon values of raw shales and the compositional data from *Table 3*, estimates of the heating values of Green River and New Albany Formation oil shales can be obtained.

The accuracy of heating-value estimates from the Boie equation is dependent upon the accuracy of the analytical determinations of the elemental compositions. However, with modern analytical instrumentation, such determinations are routinely good. Thus, in many instances a heating value calculated from the elemental composition will suffice and, at the same time, save costly time and effort on the part of the analyst.

ACKNOWLEDGEMENTS

The authors wish to acknowledge John Ward Smith of the Laramie Energy Research Center for providing a translation of Boie's original manuscript and many helpful discussions.

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APPENDIX III

METHOD OF CALCULATING CALORIFIC VALUE AND SPECIFIC GRAVITY OF GASEOUS FUELS

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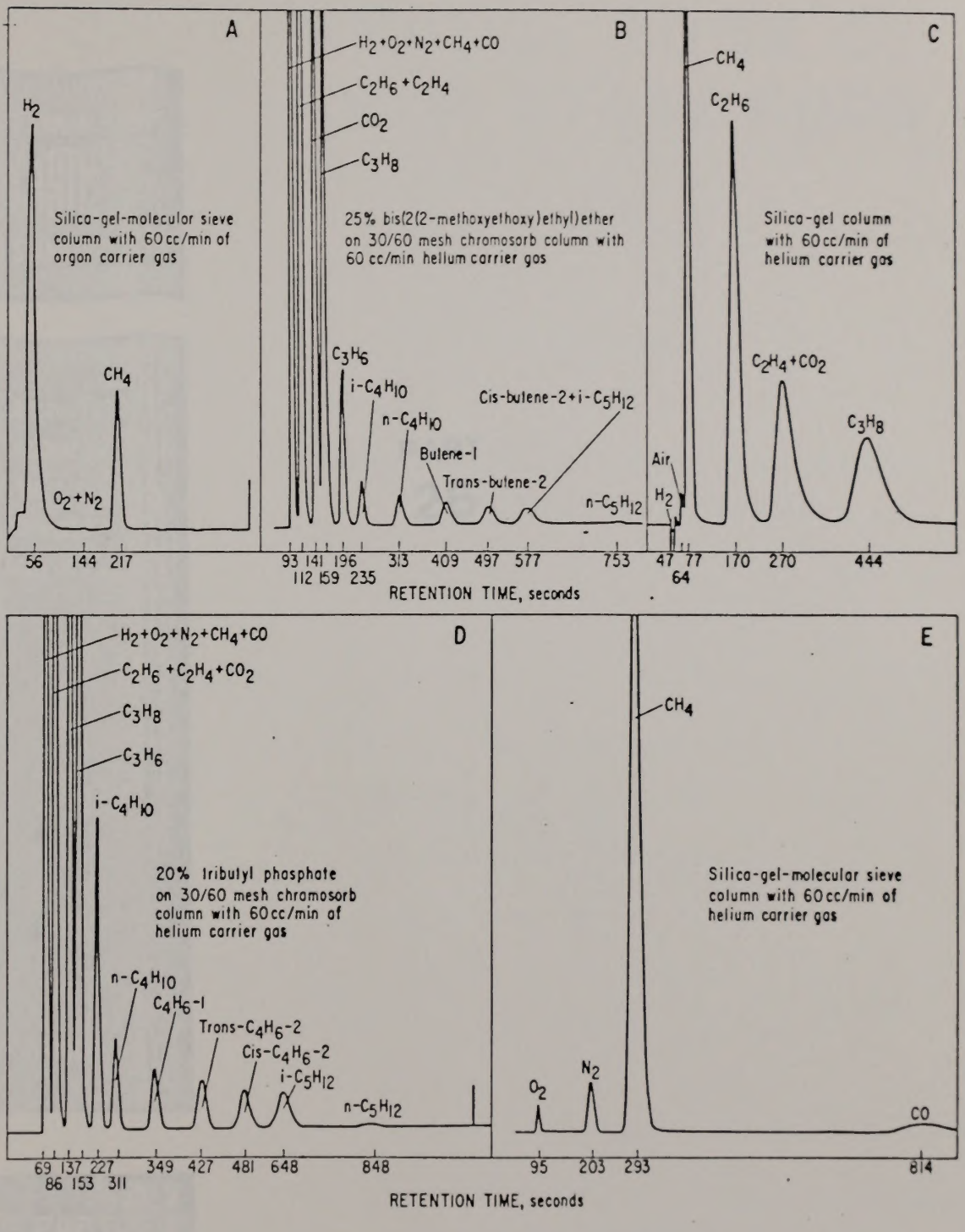
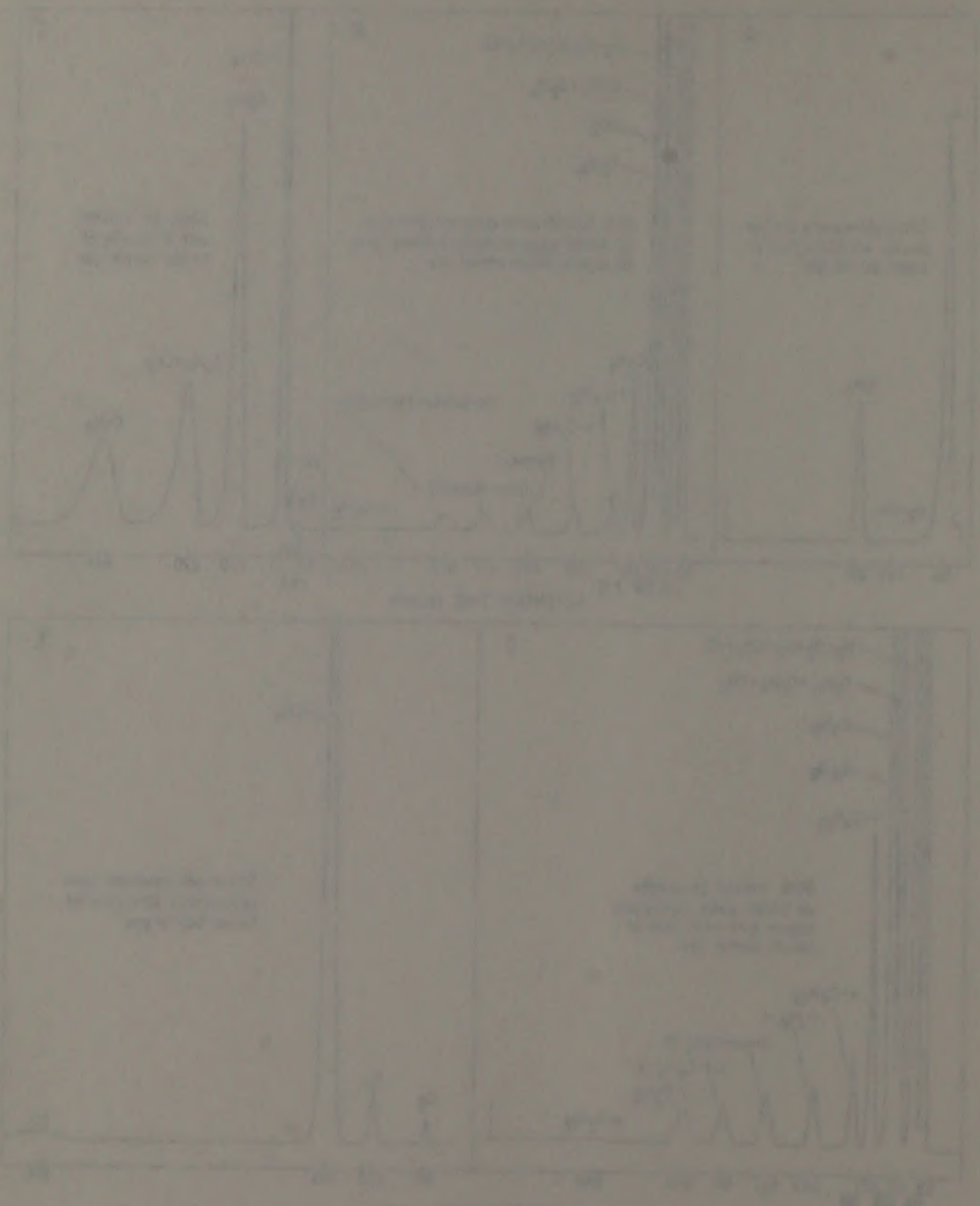
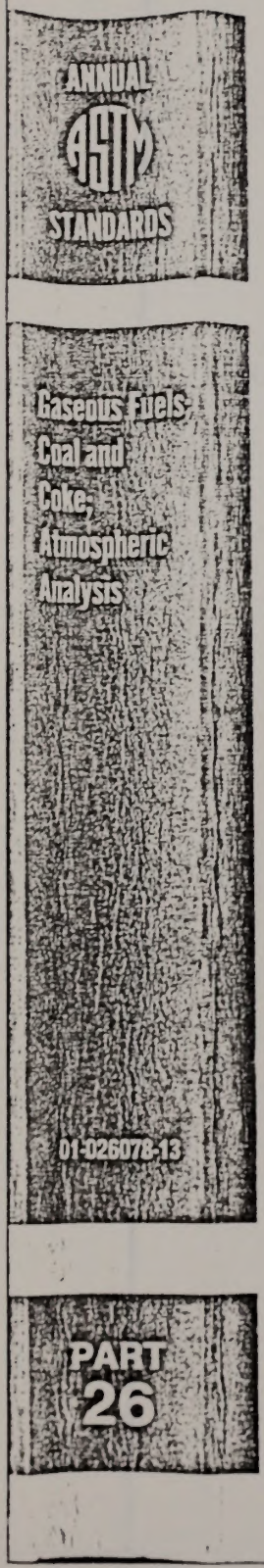


Figure III-1. - Chromatograms for Analyzing Hydrocarbon Gases.[20/]

20/ Barker, Lawrence K., 1974, Hydrogasification of In Situ Shale Oil. M. S. Thesis, Univ. Wyo., Laramie, Wyo., p. 57. (May).

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Standard Method of CALCULATING CALORIFIC VALUE AND SPECIFIC GRAVITY OF GASEOUS FUELS[1]

This Standard is issued under the fixed designation D 3588; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval.

1. Scope

1.1 This method describes the calculation of calorific value and specific gravity of gaseous fuel from its composition. It is applicable to all common types of utility gaseous fuels (for example dry natural gas, reformed gases, oil gas (both high- and low-Btu), propane-air, carbureted water gas, and coke oven and reort coal gas) for which suitable methods of analysis as described in Section 5 are available.

2. Applicable Documents

2.1 *ASTM Standards*:

D 1137 Analysis of Natural Gas and Related Types of Gaseous Mixtures by the Mass Spectrometer[2]

D 1717 Analysis of Commercial Butane-Butene Mixtures by Gas Chromatography[2]

D 1826 Test for Calorific Value of Gases in Natural Gas Range by Continuous Recording Calorimeter[2]

D 1945 Analysis of Natural Gas by Gas Chromatography[2]

D 1946 Analysis of Reformed Gas by Gas Chromatography[2]

D 2163 Analysis of Liquefied Petroleum (LP) Gases and Propylene Concentrates by Gas Chromatography[2]

D 2650 Test for Chemical Composition of Gases by Mass Spectrometry[3]

2.2 *Other Standards:*

ANSI Z132.1-1969, Base Conditions of Pressure and Temperature for the Volumetric Measurement of Natural Gas[4]

3. Summary of Method

3.1 The ideal gas calorific value and ideal gas specific gravity are calculated from the molar composition and the respective ideal gas values for the components; these values are then corrected to the real gas basis by means of a calculated compressibility factor.

4. Definitions

4.1 *British thermal unit*—the defined International Tables British thermal unit (symbol Btu).

NOTE 1—The defining relationships are:

$$(a)\ 1\ \text{Btu}\cdot\text{lb}^{-1} = 2.326\ \text{J}\cdot\text{g}^{-1}\ \text{(exact)}$$
$$(b)\ 1\ \text{lb} = 453.592\ 37\ \text{g}\ \text{(exact)}$$

By these relationships, 1 Btu = 1 055.055 852 62 J (exact). For most purposes the value rounded to Btu = 1 055.056 J is adequate.

4.2 *compressibility factor (z)*—the ratio of the actual volume of a given quantity of gas at a specified temperature and pressure to its volume calculated from the ideal gas law at the same conditions.

4.3 *total calorific value or gross calorific value (gross heating value) of a gas*—the number of British thermal units evolved by the complete combustion, at constant pressure, of one standard cubic foot of gas with air, the temperature of the gas, air, and products of combustion being 60°F (15.6°C) and all the water formed by the combustion reaction being condensed to the liquid state.

---

[1] This method is under the jurisdiction of ASTM Committee D-3 on Gaseous Fuels, and is the direct responsibility of Subcommittee DO3.03 on Determination of Calorific Value of Gaseous Fuels.

Current edition approved June 24, 1977. Published August 1977.

[2] *Annual Book of ASTM Standards*, Part 26.

[3] *Annual Book of ASTM Standards*, Part 24.

[4] Available from the American National Standards Institute, 1430 Broadway, New York, N.Y. 10018.

4.4 *net calorific value of a gas* – the number of British thermal units evolved by the complete combustion, at constant pressure, of 1 standard cubic foot of gas with air the temperature of the gas, air, and products of combustion being 60°F (15.6°C) and all of the water formed by the combustion reaction remaining in the vapor state.

4.5 *specific gravity* – ratio of the density of the gaseous fuel, under specific conditions of temperature and pressure, to the density of dry air, of normal carbon dioxide content, at the same temperature and pressure.

4.6 *standard cubic foot of gas* – the amount of gas that occupies 1 ft^3 (0.028 m^3) at a temperature of 60°F (15.6°C) under a pressure of 14.73 psia (101 kPa) and saturated with water vapor.

5. Methods of Analysis

5.1 Determine the molar composition of the gas in accordance with any ASTM method that yields the complete composition, exclusive of moisture, but including all other components present in amounts of 0.1 % or more, in terms of components or groups of components listed in Table 1, and also so that at least 98 % of the sample is reported as individual components (that is, not more than a total of 2 % reported as groups of components such as butanes, pentanes, hexanes, butenes, etc.). Any group used shall be one of those listed in Table 1 for which average values are given.

6. Calculation

6.1 Calculate the ideal gas calorific value, H, and ideal gas specific gravity, G, as follows:

$$H = x_1H_1 + x_2H_2 + \ldots x_nH_n$$
$$G = x_1G_1 + x_2G_2 + x_3G_3 + \ldots x_nG_n$$

where:

$x_1, x_2, \ldots x_n$ = mole fractions of the component, and

$H_1, H_2, \ldots H_n$ and $G_1, G_2, \ldots G_n$ = ideal gas gross calorific values and ideal gas specific gravities, respectively, of the components as given in Table 1 (dry basis).

Include any heptane and heavier paraffins and hexenes with hexanes.

6.2 Calculate the compressibility factor, z, at 60°F (15.6°C) and 14.73 psia (101 kPa) as follows:

$$z = 1 - (x_1b_1^{0.5} + x_2b_2^{0.5} + \ldots x_nb_n^{0.5})^2 + (2x_H - x_H^2)\,(0.0005)$$

where:

$b_1^{0.5}, b_2^{0.5}, \ldots b_n^{0.5}$ = summation factors for the respective components other than hydrogen, as given in Table 1, and

x_H = the mole fraction of hydrogen.

Include any hepatane and heavier paraffins and hexenes with hexanes.

NOTE 2 – The summation factors $b_i^{0.5}$ are obtained from the compressibility factors of the normally gaseous components according to the relation $b = 1 - z$, except for the components hydrogen, helium, and carbon dioxide. Pseudo values of the factor are furnished for helium and carbon dioxide. These may be used for carbon dioxide contents up to about 30 % and for helium contents up to about 1 % with no loss of accuracy. Factors for normally liquid components were obtained from compressibility factors estimated for the hypothetical gas or from gas mixture data.

6.3 Calculate real gas calorific value H_r, and real gas specific gravity, G_r, as follows:

$$H_r \text{ (saturated)} = 0.9826\ H/z \quad H_r \text{ (dry)} = H/z$$
$$G_r = 0.99959\ G/z$$

NOTE 3 – An example of the calculation is given in Table 2.

NOTE 4 – The vapor pressure of water at 60°F is 0.2561 psia. The ratio of the volume of dry gas to the volume of the same quantity of saturated gas thus is (14.73 − 0.2561)/14.73 = 0.9826. The factor 0.99959 in the calculation of specific gravity is the compressibility of dry air at 14.73 psia (101 kPa) and 60°F (15.6°C).

NOTE 5 – To convert calorific values to a cubic foot based on 60°F (15.6°C) and on standard atmosphere pressure (101.325 kPa), dry, multiply H_r, dry, by 0.99769. To convert calorific values to MJ/m^3 at the same standard conditions, multiply by 0.03759. See Method D 1826 for calculation to other pressure and temperature bases.

NOTE 6 – To calculate net calorific value proceed as in 6.1, 6.2, and 6.3 but in 6.1 use the ideal gas net calorific values of Table 1 in place of the ideal gas total calorific values.

7. Precision

7.1 Calculate the repeatability, ΔH, as follows:

$$\Delta H = [\Sigma(H - H_i)^2\,(\Delta x_i)^2]^{0.5}$$

where Δx_i is the applicable repeatability stated for each component in the method of analysis. The difference between real gas calorific values calculated from two different analyses by the same operator is expected to exceed this ΔH in only 5 % of a large number of pairs of analyses.

7.2 Calculate the reproducibility according to the same equation, but with Δx_i equal to the applicable reproducibility for each component. The difference between real gas calorific values calculated from analyses obtained in different laboratories is expected to exceed this ΔH in only 5 % of a large number of pairs of results.

NOTE 7—An example using precision statements from Method D 1945 is shown in Table 3.

NOTE 8—Three sources of error have been considered: error in calorific values of the components; error in the calculated compressibility factor; and error in the composition. The uncertainty (twice the standard deviation) of the ideal gas calorific values of components is estimated to be 0.03 %. Such errors affect the bias and thus the agreement between calculated and determined calorific values, but does not affect the precision. Error in the calculated compressibility factor will vary with composition of the gas, but for natural gas is estimated to be less than 0.03 %, and commonly is negligible compared to the error from the uncertainty in composition.

TABLE 1 Properties of Fuel Gas Components

	Ideal Gas Specific Gravity[A]	Ideal Gas Total Calorific Value,[B] Btu/ft³	Ideal Gas Net Calorific Value,[B] Btu/ft³	Compressibility Summation Factor
Hydrocarbon:				
Methane	0.5539	1012.0	911.2	0.0436
Ethane	1.0382	1772.9	1621.6	0.0917
Propane	1.5224	2523.0	2321.4	0.1342
Isobutane	2.0067	3260.1	3008.0	0.1744
n-Butane	2.0067	3269.6	3017.5	0.1825
Butanes, avg	2.0067	3265	3013	0.178
Isopentane	2.4910	4009.4	3706.4	0.2276
n-Pentane	2.4910	4018.5	3716.0	0.2377
Pentanes, avg	2.4910	4014	3711	0.233
Hexanes, avg	2.9753	4758	4405	0.283
Ethylene	0.9686	1602.9	1502.0	0.0775
Propene	1.4528	2339.0	2187.8	0.1269
1-Butene	1.9371	3087.3	2885.6	0.1749
cis-2-Butene	1.9371	3079.7	2878.0	0.1863
trans-2-Butene	1.9371	3073.4	2871.7	0.1860
2-Methylpropene	1.9371	3068.0	2866.3	0.1769
Butenes, avg	1.9371	3077	2875	0.181
1-Pentene	2.4214	3835.3	3583.1	0.230
cis-2-Pentene	2.4214	3828.2	3576.1	0.230
trans-2-Pentene	2.4214	3823.4	3571.3	0.230
2-Methyl-1-butene	2.4214	3819.2	3567.1	0.230
3-Methyl-1-butene	2.4214	3827.5	3575.3	0.230
2-Methyl-2-butene	2.4214	3812.3	3560.2	0.230
Pentenes, avg	2.4214	3824	3572	0.230
Acetylene	0.8990	1476.2	1425.7	0.0833
1;3-Butadiene	1.8675	2887.7	2736.4	0.158
1;3-Cyclopentadiene	2.2822	3362.0	3210.0	0.224
Benzene	2.6969	3750.6	3599.3	0.266
Toluene	3.1812	4485.2	4283.5	0.311
C_8 Aromatics, avg	3.6654	5224	4972	0.36
Nonhydrocarbons:				
Air	1.0000	. . .	. . .	0.0202
Carbon dioxide	1.5194	. . .	. . .	0.0640
Carbon monoxide	0.9671	321.3	321.3	0.0217
Helium	0.1382	. . .	. . .	0.017
Hydrogen	0.0696	324.9	274.5	. . .
Hydrogen sulfide	1.1765	638.6	588.2	0.0985
Nitrogen	0.9672	. . .	. . .	0.0164

[A] Ratio of molecular weight (1971) of component to that of air (28.9644).

[B] Combustion at 60°F (15.6°C); volume of a pound mole of ideal gas at 14.73 psia (101 kPa) = 378.601 ft³ (10.798 m³) on the dry basis.

[C] Source of data is the "Selected Values of Properties of Hydrocarbons and Related Compounds" from the American Petroleum Institute Research Project 44. Additional details are available from ASTM Research Report No. D03-1000.

TABLE 2 Sample Calculation

	Ideal Gas Specific Gravity, G_i	Ideal Gas Total Calorific Value, H_i	Compressibility Summation Factor, $\sqrt{b_i}$	Composition Mole Fraction, x_i	Specific Gravity Fraction, x_iG_i	Calorific Value Fraction, x_iH_i	Compressibility Fraction, $x_i\sqrt{b_i}$
Helium	0.1382	. . .	−0.017	0.0003	0.0000	. . .	0.0000
Nitrogen	0.9672	. . .	0.0164	0.0032	0.0031	. . .	0.0001
Carbon dioxide	1.5194	. . .	0.0640	0.0202	0.0307	. . .	0.0013
Methane	0.5539	1012.0	0.0436	0.8302	0.4598	840.2	0.0362
Ethane	1.0382	1772.9	0.0917	0.0745	0.0773	132.1	0.0068
Propane	1.5224	2523.0	0.1342	0.0439	0.0668	110.8	0.0059
Isobutane	2.0067	3260.1	0.1744	0.0083	0.0166	27.1	0.0014
n-Butane	2.0067	3269.6	0.1825	0.0108	0.0217	35.3	0.0020
Isopentane	2.4910	4009.4	0.2276	0.0031	0.0077	12.4	0.0007
n-Pentane	2.4910	4018.5	0.2377	0.0025	0.0062	10.0	0.0006
Hexanes	2.9753	4758	0.283	0.0030	0.0089	14.3	0.0008
				1.0000	0.6988	1182.2	0.0558

$z = (\Sigma\, x_i\sqrt{b_i})^2 + (2x_{II} - x_{II}^2)\,(0.0005)$
$= 1 - 0.0031$
$= 0.9969$

Specific gravity of mixture = 0.6988 × 0.99959/0.9969 = 0.7007.

Total calorific value = 1182.2 × 0.9826/0.9969 = 1165.2 Btu/standard ft³.

TABLE 3 Sample Collection of Precision

	Ideal Gas Total Calorific Value, H_i	Composition Mole Fraction, x_i	$H - H_i$	Repeatability		Reproducibility	
				Δx_i[A]	$[(H - H_i)\Delta x_i]^2$	Δx_i[A]	$[(H - H_i)\Delta x_i]$
Helium	0.0	0.0003	1182.2	0.0003	0.126	0.0006	0.503
Nitrogen	0.0	0.0032	1182.2	0.0005	0.349	0.0010	1.398
Carbon dioxide	0.0	0.0202	1182.2	0.0005	0.349	0.0010	1.398
Methane	1012.0	0.8302	170.2	0.003	0.261	0.0060	1.043
Ethane	1772.9	0.0745	−590.7	0.0015	0.785	0.0020	1.396
Propane	2523.0	0.0439	−1340.8	0.0005	0.449	0.0010	1.798
Isobutane	3260.1	0.0083	−2077.9	0.0003	0.389	0.0006	1.554
n-Butane	3269.6	0.0108	−2087.2	0.0005	1.089	0.0010	4.357
Isopentane	4009.4	0.0031	−2827.2	0.0003	0.719	0.0006	2.878
n-Pentane	4018.5	0.0025	−2836.3	0.0003	0.724	0.0006	2.896
Hexanes	4758	0.0030	3578.8	0.00015	0.537	0.0003	1.153
		1.0000			5.778		20.374

[A] Method D 1945.

H = 1182.2 (See Table 2).

Repeatability: $(5.778)^{0.5}$ = 2.4 Btu/ft³.

Reproducibility: $(20.374)^{0.5}$ = 4.5 Btu/ft³.

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